Methyl *tert*-Butyl Ether (MTBE) in the Aquatic Environment in Germany

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Kurzfassung (Short Summary)

Der Einsatz des Kraftstoffadditivs Methyl *tert*-butylether (MTBE) hat in den USA (1999: 9,3 Millionen t) zu erheblichen Kontaminationen von Grundwasser durch unterirdische Tankleckagen geführt. Da dies zur Schließung von Trinkwasserversorgungsbrunnen führte, wurde MTBE in einigen Bundesstaaten verboten. Darüber hinaus wird das Oxygenat in der Atmosphäre und der aquatischen Umwelt besonders in besiedelten Gebieten häufig nachgewiesen. Auch in Deutschland wird das Oxygenat eingesetzt, jedoch in geringerem Umfang.

Das Ziel der vorliegenden Arbeit war die Klärung der Frage, in welchem Ausmaß MTBE in Deutschland eingesetzt wird, und ob der Einsatz des Oxygenats in der Umwelt zu nachweisbaren Konzentrationen geführt hat. Es sollte eine empfindliche Messmethode entwickelt werden, um Oberflächenwasser in Deutschland zu analysieren. Die Ergebnisse sollten dazu dienen, einen Überblick über die MTBE-Situation in Deutschland zu erhalten und Emissionsquellen zu ermitteln.

Bedingt durch einen hohen Dampfdruck (330 hPa bei 25 °C) und einen niedrigen Siedepunkt (55 °C) evaporiert MTBE leicht aus Kraftstoffen in die Umwelt. Die hohe Wasserlöslichkeit (42 g/L bei 20 °C) des Ethers führt zu einem bevorzugten Verbleib in der wässrigen Phase. Bedingt durch die schlechte Abbaubarkeit und die geringe Retardierung im Untergrund, stellt MTBE eine persistente Verbindung im Wasser dar. Zur Toxizität von MTBE liegen widersprüchliche Angaben vor, so daß eine abschließende Bewertung zur Zeit nicht erfolgen sollte.

Mittels einer eigens hierfür entwickelten Messmethode basierend auf Gaschromatographie (GC) mit Flammenionisationsdetektion und nur einer Kapillarsäule wurden 1999/ 2000 Vergaserkraftstoffe aus dem Frankfurter Raum auf ihren MTBE-Gehalt analysiert. Die Konzentrationen schwankten von 0,3 – 0,6 Gew.-% im Normal Benzin, von 0,3 – 4,2 Gew.-% im Superkraftstoff, von 6,8 – 12,2 Gew.-% im Superplus und von 10,4 – 13,6 Gew.-% im „Optimax“-Kraftstoff. Aus den Messwerten wurde ein MTBE-Verbrauch von ca. 500.000 t in deutschen Kraftstoffen für 1999 berechnet. Dieser Wert entspricht der in anderen Arbeiten geschätzten Menge.

Für die MTBE-Analyse von Oberflächenwasser wurde eine empfindliche Messmethode durch die Kombination von Solid-Phase Microextraction und Gaschromatographie/ Massenspektrometrie (SPME/ GC-MS) entwickelt. Die Nachweisgrenze liegt bei 10 ng/L und die relative Standardabweichung bei 11 %. Die beschriebene Methode lieferte in einem

kürzlich durchgeführten Ringversuch hervorragende Ergebnisse und ist auch für höherkonzentrierte Wässer geeignet, wenn diese vorher verdünnt werden.
Im Zeitraum von 1998 – 2001 wurden 616 Proben aus Niederschlag, Flüssen, Bächen, kommunalem und industriellem Abwasser, Trinkwasser, Uferfiltrat und Oberflächenabfluß mit der SPME/ GC-MS - Methode analysiert. Die Ergebnisse der Niederschlagsmessungen zeigen, daß MTBE im Winter in Städten, im Gegensatz zu ländlichen Gebieten, in geringen Konzentrationen (bis 85 ng/L) nachweisbar ist. Schneeproben zeigen höchste Gehalte. Die MTBE-Konzentrationen in deutschen Fließgewässern, städtischem Oberflächenabfluß und kommunalem Abwasser schwanken unabhängig von der Jahreszeit von <10 – 2357 ng/L und liegen im Niedermain, Niederrhein, städtischem Oberflächenabfluß und kommunalem Abwasser in Frankfurt/ M bei ca. 100 – 250 ng/L. Sonstige Flüsse und Bäche weisen häufig Konzentrationen von ca. 50 ng/L auf. Erhöhte Konzentrationen treten in urbanen Gebieten auf. Die MTBE-Gehalte in Flüssen zeigen steigende Tendenz. Die Hauptemissionsquellen für diffuse Einträge stellen Abgase und Leckagen von Fahrzeugen und Tankstellen dar. In industriellem Abwasser wurden Stoßkonzentrationen von MTBE bis ca. 30 µg/L nachgewiesen.
Durch den Reinigungsprozess der Uferfiltration wird MTBE aus Flußwasser nicht vollständig eliminiert. Auch nach der Aufbereitung treten Spuren des Kraftstoffzusatzes im Trinkwasser auf, liegen jedoch um den Faktor 100 – 1000 unter der Trinkwasserrichtline der USA (13 µg/L). Diese Ergebnisse stellen einen Beitrag zur Vorsorge dar, da MTBE neben chlorierten Kohlenwasserstoffen die häufigste leichtflüchtige Chemikalie in der aquatischen Umwelt darstellt.
Mit Hilfe der durchgeführten Kompartiment-Modellierung (Equilibrium Criterion Model) wurde die Emission von MTBE direkt in die wässrige Phase als sehr wichtigen Faktor für die MTBE-Konzentration im Wasser ermittelt. Diese Emission wird für Deutschland im Bereich von etwa 50 t/a geschätzt. Zusätzliche, bisher unbekannte industrielle Einträge sind wahrscheinlich.

Ab dem Jahr 2005 ist aufgrund gesetzlicher Regulierungen mit derVerdopplung der MTBE-Gehalte im Kraftstoff zu rechnen. Bis dahin wird in Europa eine Entscheidung für MTBE oder für alternative Additive, wie Ethanol oder Ethyl *tert*-butylether (ETBE) anstehen.

Zusammenfassung (Summary)

Die Aufgabe der vorliegenden Arbeit war die Klärung der Frage, in welchem Ausmaß das Kraftstoffadditiv Methyl *tertiär*-butylether (MTBE) in Deutschland eingesetzt wird, und ob die Verwendung des Oxygenats in der Umwelt zu nachweisbaren Konzentrationen geführt hat. Es sollte eine empfindliche Messmethode entwickelt werden, um Oberflächenwasser in Deutschland zu analysieren. Die Ergebnisse sollten dazu dienen, einen Überblick über die MTBE-Situation in Deutschland zu erhalten und Emissionsquellen zu ermitteln.

Oxygenate sind Substanzen, die organisch gebundenen Sauerstoff enthalten (meist Alkohole und Ether) und Vergaserkraftstoffen zugesetzt werden, um deren Verbrennungsverhalten zu verbessern bzw. die Oktanzahl der Kraftstoffe zu erhöhen. MTBE stellt mit **Produktionsmengen** von 9,3 Millionen t (1999) in den USA, 3,3 Millionen t (1999) in den Ländern der Europäischen Union (EU) und 500.000 t (1999) in Deutschland, gefolgt von Ethanol (4,4 Millionen t in den USA), den wichtigsten Vertreter dar [EIA, 1999; MEF, 2001; PAHLKE ET AL, 2000]. Es ersetzt sowohl Bleitetraethyl, das nach Einführung der Katalysatoren den Vergaserkraftstoffen entzogen wurde, als auch aromatische Kohlenwasserstoffe (darunter das karzinogene Benzol), die mit für die Bildung von Smog verantwortlich sind. Von geringer Bedeutung sind bisher die Oxygenate Ethyl *tertiär*-butylether (ETBE), *tertiär*-Amylmethylether (TAME), Di-isopropylether (DIPE) und Methanol. In den USA wird MTBE seit Ende der 70er Jahre und in Deutschland seit 1985 als Oxygenat verwendet. Zu einem verstärkten Einsatz kam es 1992 in den Vereinigten Staaten durch das Inkrafttreten des Luftreinhaltungsgesetzes "Clean Air Act Amendments". Es schreibt die Verwendung von "Oxyfuel" mit 2,7 Gew.-% organisch gebundenem Sauerstoff (enspricht 15 Vol-% MTBE oder 7 Vol-% Ethanol) in Regionen vor, in denen die zulässige CO-Konzentration in der Luft überschritten wird (häufig im Winter). In den Ländern der Europäischen Union wird MTBE (in Frankreich überwiegend ETBE und in Finnland auch TAME) in erster Linie zur Regulierung der Research Oktanzahl (ROZ) hochwertiger Kraftstoffe verwendet und gesetzlich lediglich ein maximaler MTBE-Gehalt von 15 Vol.-% im Kraftstoff zugelassen. Im Rahmen dieser Arbeit wurde eine Messmethode für die Analyse von **MTBE in Kraftstoffen** basierend auf Gaschromatographie (GC) mit Flammenionisationsdetektion (FID) entwickelt. Analysierte Proben aus dem Frankfurter Raum (1999/ 2000) lieferten MTBE-Gehalte von 0,3 – 0,6 Gew.-% in Normal Benzin (ROZ = 93), 0,3 – 4,2 Gew.-% in

Super-Kraftstoff (ROZ = 96), 6,8 – 12,2 Gew.-% in Superplus und 10,4 – 13,6 Gew.-% in dem ausschließlich von der Firma Shell vertriebenen "Optimax" [ACHTEN AND PÜTTMANN, 2001A]. Zu berücksichtigen ist, dass der Superplus-Anteil an allen deutschen Kraftstoffen heute weniger als 5 % beträgt.

Erstmals hat MTBE 1996 für große Verunsicherung in der Bevölkerung gesorgt, als aufgrund unterirdischer Tankleckagen in Santa Monica (Kalifornien) MTBE-haltiger Kraftstoff das Grundwasser kontaminierte (bis 600 µg/L MTBE) und damit die Hälfte der städtischen Trinkwasser-Versorgungsbrunnen unbrauchbar machte [HAPPEL ET AL., 1998]. Nachdem weitere Schadensfälle bekannt wurden, kam es zum Verbot des Oxygenats in kalifornischem Kraftstoff ab 2003 und weitere U.S. Staaten folgten der Entscheidung bis schließlich der US-Senat das Verbot der Verwendung von MTBE ab 2005 vorgeschlug. In Deutschland wird ein akutes Risiko für die Umwelt aufgrund der – im Vergleich zu Kalifornien – niedrigeren MTBE-Gehalte im Kraftstoff und höherer Sicherheitsstandards bei den Tankanlagen vom Umweltamt ausgeschlossen [PAHLKE ET AL., 2000].

Die **Herstellung** von MTBE erfolgt durch die Addition von Methanol an Isobutylen in Anwesenheit eines sauren Katalysators. In der EU stellen die Niederlande den Hauptproduzenten mit 900.000 t/a (1997) dar [DEWITT COMPANY, 1998 AND 1999]. In Deutschland werden etwa 300.000 t bei Degussa Hüls in Marl und Miro in Karlsruhe und 244.000 t an sechs weiteren Standorten produziert [PAHLKE ET AL., 2000]. Der Einsatz als Kraftstoffzusatz erfolgt zu einem Anteil von 98,5 % und nur zu 1,5 % im industriellen und medizinischen Bereich [MEF, 2001].

MTBE ist mit einem niedrigen Siedepunkt von 55 °C und einem hohen Dampfdruck von 330 hPa (bei 25 °C) in die Gruppe der leichtflüchtigen Kohlenwasserstoffe (VOCs) einzuordnen. Es weist eine außergewöhnlich gute Wasserlöslichkeit von 42 g/L (bei 20 °C) bis 83 g/L (bei 0 °C) auf. MTBE adsorbiert praktisch weder an Sedimentpartikeln noch an organischem Material und ist im Wasser und Boden nur schlecht abbaubar, besonders unter anaeroben Bedingungen. Das Hauptabbauprodukt im Wasser ist *tertiär*-Butylalkohol (TBA) und in der Luft *tertiär*-Butylformiat (TBF), das schnell zu TBA hydrolysiert. Die Halbwertszeit in der Atmosphäre beträgt 3 - 6 d [SMITH ET AL., 1991] und umfaßt einen Europa-weiten Transport [SCHOLZ, 2001]. MTBE verdampft sehr schnell pur und aus MTBE-haltigem Kraftstoff, jedoch nur sehr langsam aus Wasser (besonders bei niedrigen

Temperaturen). Im Vergleich dazu evaporiert Benzol langsamer, wird im Untergrund retardiert und schneller abgebaut. Im Gegensatz zu Benzol sind zur Sanierung von kontaminiertem Wasser konventionelle Strippverfahren ungeeignet [EFFENBERGER ET AL., 2001].

Zur **Toxizität** von MTBE liegen widersprüchliche Angaben vor, so daß eine abschließende Bewertung zur Zeit nicht erfolgen sollte [MEHLMANN, 2001]. Einerseits ist die akute Toxizität als gering einzustufen, andererseits wurde bei hohen Konzentrationen karzinogene Wirkungen beobachtet. Es sind keine Langzeituntersuchungen bei niedrigen Konzentrationen bekannt. Die EPA stufte MTBE als „möglicherweise krebserregend für den Menschen" ein [EPA, 2001], während die Weltgesundheitsorganisation von keiner akuten Gesundheitsgefährdung ausgeht [WHO, 1998]. Die Trinkwasserrichtlinie der U.S. amerikanischen Umweltbehörde (EPA) schreibt einen Grenzwert von 13 µg/L für MTBE vor. Dieser Wert basiert in erster Linie auf dem Bereich der Geruchs- und Geschmacksschwelle (etwa 20 – 40 µg/L) von MTBE in Wasser und weniger auf gesundheitlichen Aspekten. In Deutschland wird der Ether in die Wassergefährdungsklasse 1 (gering wassergefährdend) eingestuft [KLOEPFER, 1999].

Der **Eintrag** von hohen MTBE-Konzentrationen (mg/L-Bereich) in die aquatische Umwelt kann durch Tankleckagen im Untergrund hervorgerufen werden und zu signifikanten Grundwasserkontaminationen führen [HAPPEL ET AL., 1998] (Grundwasser wurde in dieser Arbeit nicht untersucht). Weitere Eintragspfade stellen industrielle und kommunale Abwässer dar, für die es in Deutschland derzeit keine Richtlinien bezüglich MTBE gibt. Durch den hohen Dampfdruck bedingt, kann das Additiv beim Transport und Umfüllen von MTBE-haltigen Kraftstoffen oder aus deren Abgasen in die Atmosphäre und durch den Niederschlag in die Oberflächengewässer gelangen. Diese diffusen Einträge führen im oberflächennahen Grundwasser unter U.S. amerikanischen Verhältnissen maximal zu 1 µg/L [BAEHR ET AL., 1999] und sind noch wenig erforscht. Zur Situation von MTBE in der aquatischen Umwelt in Deutschland konnten bisher aufgrund mangelnder Analysendaten keine gesicherten Aussagen gemacht werden.

Die **Analytik** von MTBE in Wasser erfolgt durch GC oder Gaschromatographie/ Massenspektrometrie (GC/ MS) in Kombination mit unterschiedlichen Extraktionstechniken, wie Purge-and-Trap (P&T), Headspace-Analyse (HS) oder Solid-Phase Microextraction (SPME). Da Peaküberlagerungen (häufig mit 2-Methylpentan) bei der Verwendung eines FID

Tabelle 0-1 Analysenbedingungen von Methyl tertiär-butylether (MTBE) in Wasser mittels Headspace-Solid-Phase Microextraction (HS-SPME) und Gaschromatographie/ Massenspektrometrie (GC/ MS)

HS-SPME	
Faser	Poly(dimethylsiloxan)/ Carboxen
Probenhaltertemperatur	0 °C
Magnetischer Rührfisch	3 mm (Supelco), 895-900 U/min
Probenbehältervolumen	10 ml
Probenvolumen	4 ml
Probentemperatur	35 °C
Extraktion	Kopfraum
Einstichtiefe der Faser in Probenbehälter	0,8 cm
Extraktionszeit	30 min
NaCl-Gehalt	10 %
GC	
Gerät	Thermo Quest CE Instrum. Trace GC 2000 Series
Chromatographische Säule	SE-54 , 50 m, 5 µm Filmstärke (CS)
Trägergas	Helium, 70 kPa
Split	1:20
Liner (Innendurchmesser)	0,75 mm
Temperaturprogramm	1 min 50 °C, 10 °C/min auf 200 °C, 20 min
Injektortemperatur	260 °C
Einstichtiefe der Faser in Injektor	3,8 cm
Konditionierungszeit der Faser	10 min
MS	
Gerät	Thermo Quest Finnigan Voyager GC/ MS
Software	Xcalibur (Version 1.0)
Ionisierungsmodus	EI^+
Ionenquellentemperatur	220 °C
Interfacetemperatur	250 °C
Scan Modus und Bereich	Full Scan, 40 - 600 *m*/*z*
Interner Standard	Deuteriertes MTBE (d_3MTBE)
Gesamte Analysendauer	39 min

nicht auszuschließen sind, sollte ein Massenspektrometer als Detektor bevorzugt werden. Übliche Methoden lieferten Nachweisgrenzen bis 60 ng/L, die für Nachweise von MTBE in deutschen Oberflächenwässern zu hoch sind bzw. waren. Die Vor- und Nachteile der unterschiedlichen Extraktionstechniken und Injektionsverfahren wurden kürzlich von SCHMIDT ET AL. [2001] detailliert diskutiert.

In dieser Arbeit wurde eine empfindliche Messmethode für MTBE in Wasser mit einer Nachweisgrenze von 10 ng/L durch die Kombination von SPME und GC/ MS entwickelt [ACHTEN UND PÜTTMANN, 2000]. Die Analysenbedingungen sind in Tabelle 0-1 dargestellt. SPME erfolgt mit einer Faser aus 75 µm Poly(dimethylsiloxan)/ Carboxen und einem auf 0 °C gekühlten manuellen Probehalter zunächst direkt im Wasser. In einem zweiten Schritt wurde die Methode verbessert und die Extraktion im Kopfraum durchgeführt (HS-SPME) [ACHTEN ET AL., 2001B]. Dadurch wird die Gefahr von Matrixeffekten reduziert, die Stabilität des MS verbessert und die Haltbarkeit der Faser erhöht. Die Faser wird 30 Min. im Kopfraum über 4 mL einer kontinuierlich gerührten Wasserprobe (bei 10 Gew.-% Salzgehalt und bei 35 °C) in einem 10 mL-Probengefäß positioniert. Anschließend erfolgt die Desorption von MTBE und anderen VOCs von der Faser im Injektor des GC/ MS bei 260 °C für 10 Minuten. Deuteriertes MTBE dient als interner Standard. Linearitäten von R^2 >0,9991 im Kalibrierungsbereich von 20 – 5000 ng/L und R^2 >0,9916 bei 20 – 100 ng/L werden, inklusive Blindwerte, gemessen. Die relative Standardabweichung von 10 % für Langzeitmessungen (100 ng/L), 11 % für Kurzzeitmessungen (20 ng/L) und Wiederfindungsraten von 83 –118 % bei 100 ng/L werden erreicht. Die beschriebene Methode hat in einem kürzlich durchgeführten Ringversuch hervorragende Ergebnisse geliefert [SCHUHMACHER UND FÜHRER, 2001].

Mit der beschriebenen Methode wurden von Dezember 1998 bis März 2001 eine Anzahl von 616 Proben aus Niederschlag, Flüssen, Bächen, Abwasser, Trinkwasser, Uferfiltrat und Oberflächenabfluß auf ihren MTBE-Gehalt analysiert. In Tabelle 0-2 sind die Ergebnisse der MTBE-Messungen in der aquatischen Umwelt zusammengefaßt.

Die Ergebnisse von 119 untersuchten **Niederschlagsproben** 17 städtischer und ländlicher Lokationen in Deutschland zeigen MTBE-Gehalte ausschließlich in den Wintermonaten mit maximal 85 ng/L [ACHTEN ET AL., 2001A]. Dies ist auf den atmosphärischen Abbau in der wärmeren Jahreszeit zurückzuführen. MTBE-Emissionen von Kraftfahrzeugen stellen eine wichtige diffuse Quelle dar, da in Städten das Oxygenat im Niederschlag öfter (86 %, n = 78), als in ländlichen Regionen (18 %, n = 42) nachweisbar ist. In Frankfurt/ M lagen von

September 2000 bis März 2001 49 % (n = 17) der Messwerte im Bereich von 30 – 85 ng/L. Der Vergleich der MTBE-Konzentrationen mit Lufttemperaturen zeigt messbare Gehalte überwiegend bei niedrigen Temperaturen (unter 10 –15 °C), wie aus den physikalisch-chemischen Eigenchaften von MTBE zu erwarten ist. Durchschnittlich wurde bei einer Temperaturabnahme von 5 °C auf 2 °C ein Anstieg der MTBE-Konzentrationen von 23 auf 33 ng/L der nachweisbaren Gehalte ermittelt. Das bekannte Phänomen, dass Schnee aufgrund seiner erhöhten Oberfläche und Verweilzeit in der Atmosphäre gasförmige organische Bestandteile besser aufnimmt als Regen [WANIA ET AL., 1998] konnte für MTBE bestätigt werden. Erhöhte Konzentrationen des Ethers wurden außerdem im ersten Niederschlag nach längeren Trockenperioden gemessen (wash-out-effect).

In den letzten drei Jahren wurden 355 Proben aus **Fließgewässern** unterschiedlicher Größe in Deutschland auf MTBE analysiert. Die Konzentrationen schwanken von <10 – 2357 ng/L, liegen meist (32 %) jedoch im Bereich von 50 – 200 ng/L [ACHTEN ET AL., 2002B]. Die höchsten durchschnittlichen MTBE-Gehalte werden im Rhein von Karlsruhe bis Wesel (etwa 250 ng/L), Niedermain (etwa 150 ng/L), in der Weser und in städtischen Bächen (etwa 100 ng/L) erreicht. Gewässer wie der Rhein oberhalb von Karlsruhe, Obermain, Elbe, Neckar, Kanäle und ländliche Bäche sind durch Konzentrationen <100 ng/L gekennzeichnet und in der Donau und der Oder konnte kein MTBE nachgewiesen werden. Städtische Bäche ohne signifikanten industriellen Einfluß weisen typischerweise Gehalte von etwa 50 ng/L auf. Sie werden zu einem geringen Anteil (20 %) durch MTBE aus dem Niederschlag selbst und größtenteils durch Kontakt mit Kraftfahrzeugen, Straßenbelägen, Vegetation, u.a. während eines Niederschlagsereignisses hervorgerufen. Die durchschnittliche MTBE-Konzentration von 12 städtischen **Oberflächenwasserproben (urban runoff)** liegt im Bereich von 100 – 200 ng/L, jedoch liegt der tatsächliche Mittelwert vermutlich höher. Sie ist vergleichbar mit denen im Niederrhein, Niedermain und städtischen Bächen. Daraus resultiert, dass zusätzliche Einträge erforderlich sind, um die gemessenen Gehalte in den Flüssen zu erklären, da städtischer Oberflächenabfluß in die Flüsse gelangt und dort stark verdünnt wird. Die Ergebnisse zeigen erhöhte MTBE-Konzentrationen in städtischen Gebieten, die neben erhöhtem Fahrzeugaufkommen auch durch industriellen Einfluß hervorgerufen werden. Potentielle Eintragsquellen sind Abwässer aus kommunalen und industriellen Kläranlagen, Verluste beim Kraftstofftransport und Leckagen an Tankanlagen in Flußnähe. Analysiertes **Abwasser** aus kommunalen Kläranlagen (67 Proben) im Frankfurter Raum ergibt ein vergleichsweise niedrigen mittleren MTBE-Gehalt von etwa 150 ng/L in Abläufen.

Tabelle 0-2 Ergebnisse der Analytik von Methyl tert-butylether (MTBE) in der aquatischen Umwelt in Deutschland (n.n. bedeutet nicht nachweisbar bzw. <10 ng/L und geht mit 10 ng/l in Mittelwerte ein. Für eine vereinfachte Darstellung wird in dieser Arbeit aufgrund der Analysenergebnisse die Trennung zwischen Ober- und Niederrhein oberhalb von Karlsruhe vorgenommen)

Proben		Proben-anzahl	MTBE-Konzentration [ng/L]			
			Minimum	Mittelwert	Median	Maximum
Niederschlag	städtisch	76	n.n.	26	15	85
	ländlich	43	n.n.	14	10	58
Oberflächenabfluß	städtisch	12	30	204	114	1 174
Oberrhein		8	13	84	69	195
Niederrhein		80	52	278	254	579
Obermain		4	n.n.	26	23	47
Niedermain		116	n.n.	186	111	2 357
Elbe		23	n.n.	48	34	123
Donau		3	-	n.n.	-	-
Neckar		1	-	15	-	-
Weser		2	89	126	126	162
Oder		1	-	n.n.	-	-
Kanäle		6	28	83	52	204
Bäche	städtisch	79	n.n.	164	47	2 267
	ländlich	38	n.n.	26	12	198
Kommunale Kläranlagen	Zuläufe	46	21	254	196	1 268
	Abläufe	21	n.n.	231	80	1 229
Industrielle	Abläufe	19	10	2 340	51	28 422
Uferfiltrat	(Rhein, Main)	22	n.n.	88	84	250
Trinkwasser aus Uferfiltrat	(Rhein, Main)	16	n.n.	38	42	110

Ein großer Anteil der gemessenen MTBE-Konzentrationen in Flüssen wird wahrscheinlich durch den Transport und der Lagerung von Kraftstoffen aber auch durch Verluste aus der chemischen Industrie hervorgerufen. Diese Vermutung wird durch einen gemessenen maximalen MTBE-Gehalt im Rheinwasser (383 ng/L) in Leopoldshafen/ Karlsruhe bei einer Stichtagsmessung erhärtet, denn dort sind mehrere Raffinerien und ein Hauptproduzent von MTBE angesiedelt. Weiterhin deuten eine geringe Anzahl (19 Proben) von gemessenen

industriellen Abläufen der chemischen Industrie im Frankfurter Raum auf die wichtige Bedeutung dieser Einträge hin. Neben einem mittleren MTBE-Gehalt bei 90 % der Proben von etwa 100 ng/L ergeben 2 Analysen Konzentrationen von 15 – 30 µg/L. Die große Varianz der gemessenen Konzentrationen im Main bei Frankfurt unabhängig vom Jahresrhythmus (im Gegensatz zum Verhalten im Niederschlag) sind dadurch erklärbar. Die Messwerte der Fließgewässer zeigen eine Tendenz zu steigenden MTBE-Konzentrationen von 1999 – 2001. Aus den Ergebnissen läßt sich folgern, daß MTBE größtenteils über kommunale Kläranlagen und industrielle Abwässer in die Fließgewässer eingetragen wird und nur zu einem geringen Anteil durch MTBE-haltigen Niederschlag. Dies erklärt auch die niedrigsten Gehalte in der Donau und der Oder, da der Abwassereintrag dort deutlich geringer ist, als in den Flüssen Rhein oder Main.
Weitere MTBE-Messungen von Oberflächenwasser wurden kürzlich von BRAUCH ET AL. [2000A] (125 Proben) und EFFENBERGER ET AL. [2001] (17 Proben) durchgeführt. Sie bestätigen grundsätzlich die Ergebnisse dieser Arbeit.

Die Nachweise von MTBE in Oberflächenwasser in Kombination mit der bekannten persistenten Eigenschaft von MTBE in Wasser führten zu der Fragestellung, ob im **Trinkwasser**, das aus **Uferfiltrat** gewonnen wird, MTBE nachweisbar ist. Die Analysen von Niederrhein- und Niedermainuferfiltrat (22 Proben) ergeben einen mittleren Gehalt von etwa 80 ng/L MTBE. Dies zeigt, dass das Oxygenat auch bei sehr niedrigen Konzentrationen im Flusswasser durch den Reinigungsprozess der Uferfiltration nicht vollständig eliminiert wird, vergleichbar mit den Schadstoffen Ethylendiamin-tetraessigsäure (EDTA) oder adsorbierbaren organischen Halogenen (AOX). In beiden Regionen zeigte aufbereitetes Trinkwasser (16 Proben) einen mittleren Gehalt von etwa 40 ng/L (<10 – 110 ng/L). Die gemessenen MTBE-Gehalte stellen Spurenkonzentrationen dar und bleiben um den Faktor 100 - 1000 unter der Trinkwasserrichtlinie in den USA von 13 µg/L. Sie stellen einen Beitrag zur Vorsorge dar, da MTBE neben den chlorierten Kohlenwasserstoffen die häufigste Chemikalie in der aquatischen Umwelt darstellt [CLAWGES ET AL., 2000] und auch dann noch viele Jahre nachweisbar sein wird, wenn es nicht mehr eingesetzt wird.

Die Untersuchung des Verhaltens von MTBE in der Umwelt mit dem **Kompartiment-Modell EQC** [MACKAY, 2001] hat eine Massenverteilung von 87 % in der Luft und 13 % im Wasser bei 10 °C im Gleichgewicht ergeben. Um den **Abbau von MTBE in Oberflächenwasser** abzuschätzen, wurde ein Batch-Versuch mit Wasser aus dem Main bei

Frankfurt/ M durchgeführt und ergab Halbwertszeiten von ca. 80 – 120 d (bei 18 °C) und etwa eineinhalb Jahren (bei 4 °C).
Aquatische MTBE-Konzentrationen zeigen eine hohe Sensitivität bezüglich direkter Emissionen ins Wasser. Sie ergeben sich fast ausschließlich (98,5 %) daraus. Dagegen setzen sich atmosphärische MTBE Konzentrationen aus einem evaporierten Anteil aus dem Wasser und aus direkten Emissionen in die Luft zusammen.
Für 1999/ 2000 werden die aquatische Emission in Deutschland von etwa 50 t/a und die mittlere Oberflächenwasserkonzentration von 50 ng/L MTBE geschätzt. Daraus ergeben sich deutsche Jahresmittelkonzentrationen des Ethers von 19 ng/L im Wasser und 167 ng/³ in der Luft unter den Randbedingungen des Modells (u.a. 10 % Wasseroberfläche). Die Gehalte zeigen eine deutliche Temperaturabhängigkeit mit erhöhten Werten bei niedrigen Temperaturen (25 – 50 %). Es bleibt unklar, ob die unterschiedlichen resultierenden MTBE-Konzentrationen im Wasser für Deutschland durch Überschätzung des Mittelwertes aus Analysendaten, durch unzutreffende Annahmen des Modells für Deutschland (u.a. 2,2 % Wasseroberfläche) und/ oder durch Unterschätzung der Einträge begründet sind. Letzteres ist wahrscheinlich. Mögliche zusätzliche Emissionen stellen Verluste durch Kraftstofftransport auf Flüssen oder Kraftstofflagerung in der Nähe von Fließgewässern dar und zusätzliche Analysen sind notwendig.

MTBE wird wahrscheinlich für einige Dekaden in der Umwelt verbleiben. 15 Jahre nach Einführung des Ethers als Kraftstoffadditiv ist es in städtischem Niederschlag im Winter und in Oberflächenwasser unabhängig von der Jahreszeit nachweisbar. Die Hauptemissions-quellen für diffuse Einträge stellen Abgase und Leckagen von Fahrzeugen sowie Tankstellen dar. Das Oxygenat stellt mit den leichtflüchtigen chlorierten Kohlenwasserstoffen (LCKW) die am häufigsten nachgewiesene organische Verbindung in Fließgewässern dar. Die MTBE-Konzentrationen in städtischen Bächen ohne industriellen Einfluß, Oberflächenabfluß und städtischer Luft sind in Deutschland etwa 6 - 7-fach niedriger als in den U.S. Staaten wie New Jersey und zeigen eine steigende Tendenz. Der Nachweis von MTBE-Spuren in Trinkwasser, das aus Uferfiltrat hervorgeht, ist zwar heute nicht besorgniserregend, jedoch ist aufgrund des vorgeschriebenen Maximalgehaltes der aromatischen Kohlenwasserstoffe im Kraftstoff von 35 % (w/w) ab dem Jahr 2005 eine Verdopplung der MTBE-Gehalte zu erwarten.
Alternative Oxygenate wie ETBE, das in Frankreich eingesetzt wird, evaporiert zu einem geringeren Teil und hat dadurch einen umweltrelevanten Vorteil gegenüber MTBE, jedoch zeigt es vergleichbar schlechte Abbaubarkeit und wurde ebenfalls bereits im Trinkwasser

nachgewiesen [LA VOIE DU NORD, 1999]. Ethanol dagegen, die vermutlich zukünftige Alternative in den USA, ist eine mikrobiell sehr leicht abbaubare Verbindung. Dies führt jedoch dazu, dass die karzinogene Kraftstoffkomponente Benzol in Grundwasserschadensfällen durch Ethanol-haltigen Kraftstoff schlechter abgebaut wird. Darüber hinaus sind hohe Investitionen für den Vertrieb dieses Kraftstoffs nötig, da die hygroskopische Eigenschaft von Ethanol zu Entmischungen führt und aus diesem Grund separate Lagerung von Kraftstoff und Ethanol bis zur Auslieferung an die Tankstellen erfordert. Der Ersatz von MTBE durch Ethanol birgt politische und wirtschaftliche Konflikte, da MTBE ein Produkt der Petrochemischen Industrie und Ethanol aus der Vergärung von Pflanzenmaterial (Bioalkohol) von der Agrarindustrie hergestellt wird.

Die wichtigste Schlussfolgerung aus dem MTBE-Konflikt und seinen Vorgängern Bleitetraethyl und Benzol ist, dass eine Chemikalie nicht als Bestandteil eines Produkts zum Einsatz kommen sollte, das vom Mensch in der Umwelt fein verteilt und verbreitet wird, ohne vorher alle umweltrelevanten Aspekte detailliert zu untersuchen und zu bewerten. Bis zum Jahr 2005 wird in Europa eine Entscheidung für einen der drei Wege anstehen.

Introduction

Since SQUILLACE ET AL. and DELZER ET AL. first comprehensively reported about the occurrence of the gasoline additive methyl *tertiary*-butyl ether (MTBE) in groundwater and urban runoff in the United States of America (U.S.) in 1996, the fuel additive has internationally become subject of discussion.

MTBE is the most important compound from the group of oxygenates that replace tetraethyl lead and aromatic hydrocarbons. Oxygenates are organic molecules, mostly ethers or alcohols, that are added to gasoline for the increase in organically bond oxygen which leads to cleaner burning of the gasoline and an increase in the research octane numbers (RON) and motor octane numbers (MON). Octane numbers indicate the resistance of gasoline towards self-ignition. The RON of gasoline components or gasoline is measured at low speed, less load and during acceleration whereas the MON is determined at high speed and higher load. The use of MTBE leads to a reduction of emissions which has contributed to significant smog reduction in areas of high traffic density such as Los Angeles, U.S.. Emissions of CO (16 - 23 %) and hydrocarbons (18 %) decrease if oxygenated gasoline is burnt in the engine, compared to gasoline without the addition of oxygenates. However, emissions of aldehydes (e.g. formaldehyde) increase and the NO_X emissions are not significantly influenced by the addition of oxygenates to gasoline [SCHIFTER ET AL., 2001].

Unfortunately, MTBE is characterized by an unfavorable combination of properties for the environmental impact. Its high vapor pressure and low boiling point lead to easy evaporation from oxygenated fuel into the atmosphere. If reformulated gasoline contacts water, the high water solubility, poor biodegradability and essentially no adsorption ability to particles of MTBE lead to significant and persistent concentrations of the ether in the aquatic environment. This is even more of a concern, as it has low odor and taste thresholds and its toxicity should not finally be evaluated.
At produced amounts of 9.3 mio t/a in the U.S., 3.3 mio t/a in the European Community and 0.5 t/a in Germany in 1999, MTBE belongs to the group of organic chemicals with highest production rates. In some regions of the U.S. up to 15 % (w/w) of MTBE is used in gasoline

following the implemented law for air quality "Clean Air Act Amendments" in 1992. The average concentration in gasoline in Europe and Germany is in the range of 1 – 2 % (w/w). In areas where oxygenated gasoline is used, the combination of its properties and high used amounts are the reason for the fact that it is one of the most often detected compounds in the environment [CLAWGES ET AL., 2000]. Amounts in the µg/L - mg/L range of the oxygenate have been detected in groundwater that is in some cases used for the drinking water production (e.g. in Santa Monica, California, where half of the drinking water wells had to be closed due to MTBE contamination [HAPPEL ET AL., 1998]). Point-sources such as oxygenated gasoline leaking from underground storage tanks (LUSTs) are mostly responsible for these high concentrations. However, groundwater was not investigated in this study and is subject of a current study at the Institute [KOLB, 2001]. Another pathway of the MTBE transport into the aquatic environment is represented by non-point source emissions that are related to all patterns of oxygenated gasoline use and transport. DELZER ET AL., [1996] first reported of measured MTBE concentrations in the ng/L - µg/L range in overland runoff in the U.S. indicating the existence of non-point source emissions. To date, the extent of affected water resources used for the drinking water production is being investigated in the U.S. [CLAWGES ET AL., 2001].

Due to the heavy drinking water contamination, some states of the U.S. (e.g. California) stopped the use of the ether as an oxygenate with the early years of this millenium and the government recommended to phase-out or significantly reduce its nationwide use as soon as possible. Alternatives like ethanol are discussed. In Europe, only little is known about MTBE concentrations in the environment [MEF, 2001] and the first conclusion from the final draft version of the risk assessment for the European Comission was the call for more information regarding emissions into surface water to be able to characterize risks to the aquatic ecosystem. In Germany, the Umweltbundesamt declared that the use of MTBE in the country does not represent an acute risk for the environment [PAHLKE ET AL., 2000]. This decision was not based on measured MTBE concentrations in the environment.

Common analytical methods using purge-and-trap or direct aqueous injection were reported not to detect less 50 ng/L of MTBE in aqueous samples [RAESE ET AL., 1995; ROSE ET AL., 1998; CHURCH ET AL., 1997]. These methods could not be applied for the analysis of MTBE in surface waters in Germany due to its low concentration (particularly at the beginning of this study in 1998).

In 1998, MTBE was an unknown contaminant in Germany and only very little information about produced and used amounts were available. MTBE concentrations measured in the German environment were not published.

The first objective of this study was to investigate, if MTBE is of any environmental concern in Germany. By use of common analytical methods, the oxygenate was detected in water from the Main river but could not be quantified due its low concentration. Therefore, the advanced aim was the development of a more sensitive analytical method than reported. In a third step, the more sensitive method could be used for the analysis of various environmental water samples to give an overview of the impact of the MTBE use on the aquatic environment in Germany. The final objective was the investigation of emission sources, pathways and the evaluation of the MTBE situation in Germany.

1 USE, HISTORY, POLITICAL AND LEGAL ASPECTS OF METHYL *TERT*-BUTYL ETHER (MTBE)

1.1 Use, History and Political Aspects of MTBE

1.1.1 United States of America (U.S.)

Since the first automobiles were constructed, petroleum refiners have worked on improved combustion efficiency, usually by the addition of octane-enhancing fuel additives. Industrial ethanol, traditionally manufactured by the fermentation of plant material was used originally. However, it was taxed for some time in exactly the same manner as beverage alcohol and the moral taint associated with whiskey production extented to industrial ethanol [JACOBS ET AL., 2001]. At that time, industrial ethanol was added small amounts of a poisonous substance in order to prevent its consumption. Tetraethyl lead became the favorite substitute of choice for refiners. It took up less space in the gas tank and did not suffer, as ethanol did, from an association with an external moral issue – until the 1970s, when its negative environmental effects became widely recognized and denounced. It also damaged the catalysts of automobiles. Finally, in 1979, alkyl lead additives were banned [POWERS ET AL., 2001]. Again, another solution to overcome the problem of knocking-effects in the engine had to be found and methyl-*tert* butyl ether (MTBE) seemed to be the key compound in the late 1970‘s. The MTBE use as additive shows several advantages like its high motor octane number of 102, significant reduction in emissions of carbon monoxide (CO) and hydrocarbons, easy and cheap production at the refinery from by-products and easy blending characteristics with gasoline (it can be transferred through existing pipelines). In addition, it is not beverable and atoms of heavy metals are not included in the molecular structure. The positive effects of the MTBE use for CO and ozone reductions in urban air were the reason for the implementation of the "Clean Air Act Amendments" in 1992. The standards prescribe the addition of at least 2 % (w/w) of organically bond oxygen to the fuel, which is about 10 % (w/w) of MTBE in winter, if CO emissions regionally exceed national standards. For the reduction of CO emissions, MTBE was selected by some gasoline producers for the production of „oxygenated fuel“ (oxyfuel, 2.7 % (w/w) of oxygen) that allow the more complete combustion of gasoline hydrocarbons. For reduced ozone formation, MTBE has been used to produce „reformulated gasoline“ (RFG, 2.0 % (w/w) of oxygen), which is low in the potent human carcinogen benzene and other aromatic compounds. The use of RFG lowers emissions of unburned

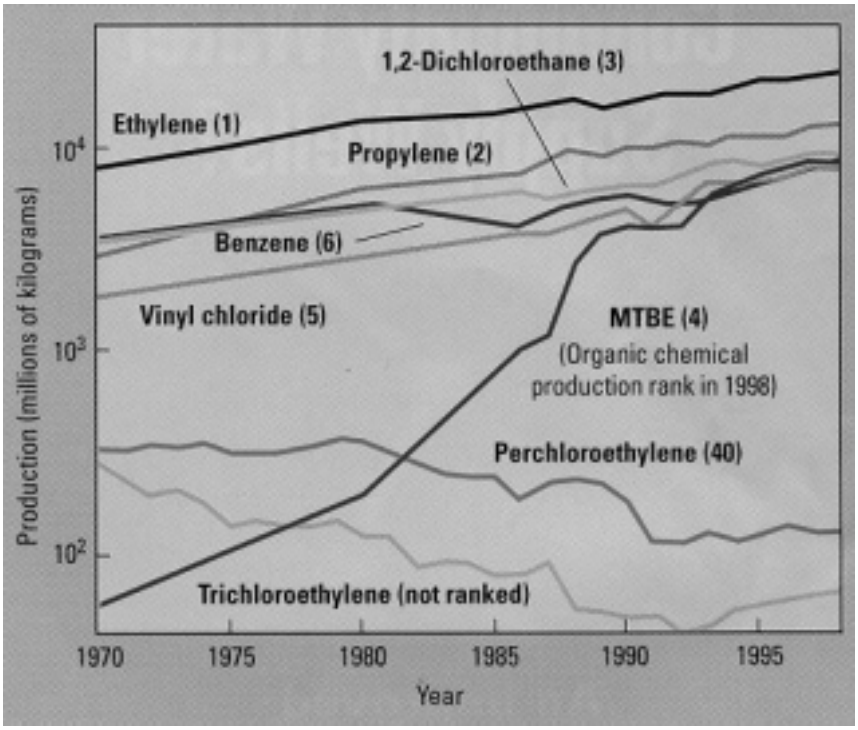


Figure 1-1 Organic chemical production in the U.S. from 1970 – 1998 [JOHNSON ET AL., 2000]. Production of methyl tert-butyl ether (MTBE) has grown dramatically since 1970, and it now ranks fourth overall among organic chemicals.

aromatic compounds and therefore the formation of ozone in the air [JOHNSON ET AL., 2000]. Since 1995, the oxygenate has been used year-round in several cities of the U.S.. The MTBE and ethanol amounts produced in America increased dramatically up to 9.3 mio t and 4.4 mio t in 1999, respectively [EIA, 1999] (Figure 1-1). Being ranked after ethylene, propylene and 1,2-dichloroethane, the oxygenate represents the fourth most produced organic chemical in the U.S.. First health complaints of workers at refineries in Fairbanks, Alaska, due to MTBE exposition and primary detections of the ether in urban runoff and groundwater were reported at the same time in the early 1990‘s. Concern regarding MTBE reached statewide levels in 1996 when in California seven wells supplying 50 % of the drinking water for the city Santa Monica were removed from service because of MTBE concentrations as high as 600 µg/L. One year later, the U.S. Geological Survey first reported about the unfavorable properties and behavior of the oxygenate in the environment [SQUILLACE ET AL., 1997A AND B]. During the following years, the extend of the MTBE contamination of groundwater due to leakage from underground storage tanks, lake water due to the use of jet-skis and generally, air and water in urban areas due to high traffic density was revealed. At the national level, it

was stated that between 5 and 10 % of communitiy drinking water supplies in high MTBE use areas show at least detectable concentrations of the oxygenate, and about 1 % of those systems are characterized by levels of this compound that are above 20 µg/L [BLUE RIBBON PANEL, 1999], where the odor and taste of MTBE is perceived by most people. To date, the extent of affected groundwater and surface water used for the drinking water production is being investigated in the U.S. [CLAWGES ET AL., 2001].

Some states reacted towards the alarming data presented. In 1999, the governor of California announced the prohibition of any MTBE concentrations in Californian gasoline from 2003 on. However, this prohibition may be delayed by one or two years [EFOA, 2001]. The state of Maine rejected the "Clean Air Act Amendments" and the Blue Ribbon Panel, a committee of the government, recommended a substantial reduction of MTBE nationwide [BLUE RIBBON PANEL, 1999]. In March 2000, the U.S. Environmental Protection Agency (EPA) issued a regulatory announcement stating its consideration of a limit or ban on the use of MTBE as fuel additive. In October, the U.S. Senate environmental and public works committee recommended a ban of MTBE beginning in 2005 which could have serious impact on gasoline prices and would damage the economy of the oil industry in the U.S. [MARXSEN, 2001].

The oxygenate ethyl *tert*-butyl ether (ETBE) is used to smaller amounts in the U.S. [KATZEN ET AL., 1997]. Ethanol, again, has been proposed as the possible substitute of choice in the future. It is already widely used in some U.S. states at concentrations of approximately 6 - 10 %, in Canada and in Brazil. Ethanol made by fermentation of corn has become an increasingly important fuel additive in the U.S. over the past decade. It can be produced from the conversion of sugars, starches or cellulosics by advanced combinations of acid and enzyme technology. Farm state lawmakers push the MTBE ban [ANONYMOUS, 2001A] because agricultural producers would significantly benefit from these plans and the production of renewable biomass fuels would also be promoted. The use of ethanol as substitute would lead to sharp hikes in gasoline prices. Even in the Midwest Cornbelt, ethanol owes to the fuel's subsidized status, otherwise it could not compete with other, petroleum-based fuel additives [MARXSEN, 2001].

A detailed summary of the economic aspects of the ethanol market is published by RASK [1998]. A consultant of the DeWitt Company, an MTBE producer, does not believe that total conversion from MTBE to ethanol is a realistic possibility by the end of 2002 and the schedule will have to be relaxed. Conversion to ethanol calls for investments of up to

$ 2 - 10 billions and feasibility studies of most MTBE producers resulted in pilot plants running on iso-octane. Producers say, that replacing MTBE with iso-octane is possible within a reasonable timeframe [ANONYMOUS, 2001C; MARXSEN, 2001]. The most readily available alternative, MMT (methylcyclopentadienyl manganese tricarbonyl), is currently not widely accepted. Recently, dimerized isobutene has been proposed as further alternative to MTBE produced from isobutene [KOLAH ET AL., 2001].

Most MTBE in the world is used in the U.S. (Figure 1-2) where it was introduced earlier compared to other contries. The total world-wide production capacity in 1994 was 20.6 mio t [ECOTOC, 1997]. In Asia, an increase in the MTBE use from 2.3 mio t in 1999 to 5.1 mio t in 2010 is assumed [OFA, 1999]. In Mexico, high amounts of MTBE are used (5 – 7.5 % (v/v)) [SCHIFTER ET AL., 2001] besides the oxygenates *tert*-amyl methyl ether (TAME) and next-TAME (C_4-C_7 tertiary alkyl methly ethers) at a capacity of 1.2 mio t/a (2001).

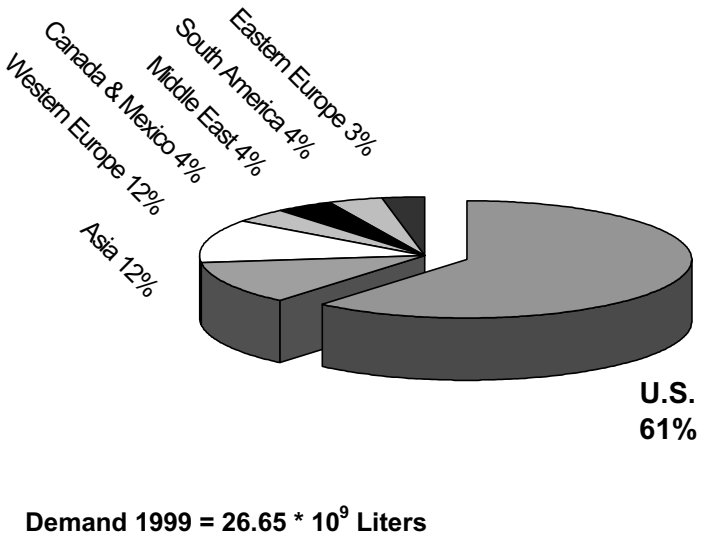


Figure 1-2 Worldwide demand of methyl tert-butyl ether (MTBE) (DeWitt Company) [THAYER, 2000].

1.1.2 European Union (EU)

The amounts of MTBE used in Western Europe are with 12 % of the total production much lower compared to the U.S. (Figure 1-2). In 1997, the total MTBE amount produced and consumed in the European Union (EU) were 3.0 and 2.13 mio t/a and prospected amounts for 1999 are 3.3 and 2.65 mio t/a, respectively [MEF, 2001]. Most MTBE is used in Italy, Spain and Germany (Figure 1-3). Large amounts are produced in the Netherlands but used elsewhere. In Finland, Belgium and Great Britain, the oxygenates TAME and next-TAME are also used and the capacities were 110,000 t/a (1996), >140,000 t/a (1988) and <240,000 t/a (1987), respectively. In France, MTBE has been partially replaced by ethyl *tert*-butyl ether (ETBE) since 1990 but also blends of MTBE, ETBE and TAME are used [RIPPEN, 2001; KHAROUNE ET AL., 2001]. In Spain, Sweden, the Netherlands and Italy, new ethanol production units are being built that allow MTBE production to be converted to ETBE [WALKER, 1999; ANONYMOUS, 2000A]. The average MTBE concentrations in gasoline are highest in Finland, Belgium and Spain. In Figure 1-3, produced amounts of ETBE are probably included although it was not described by the authors [DEWITT COMPANY, 1998;

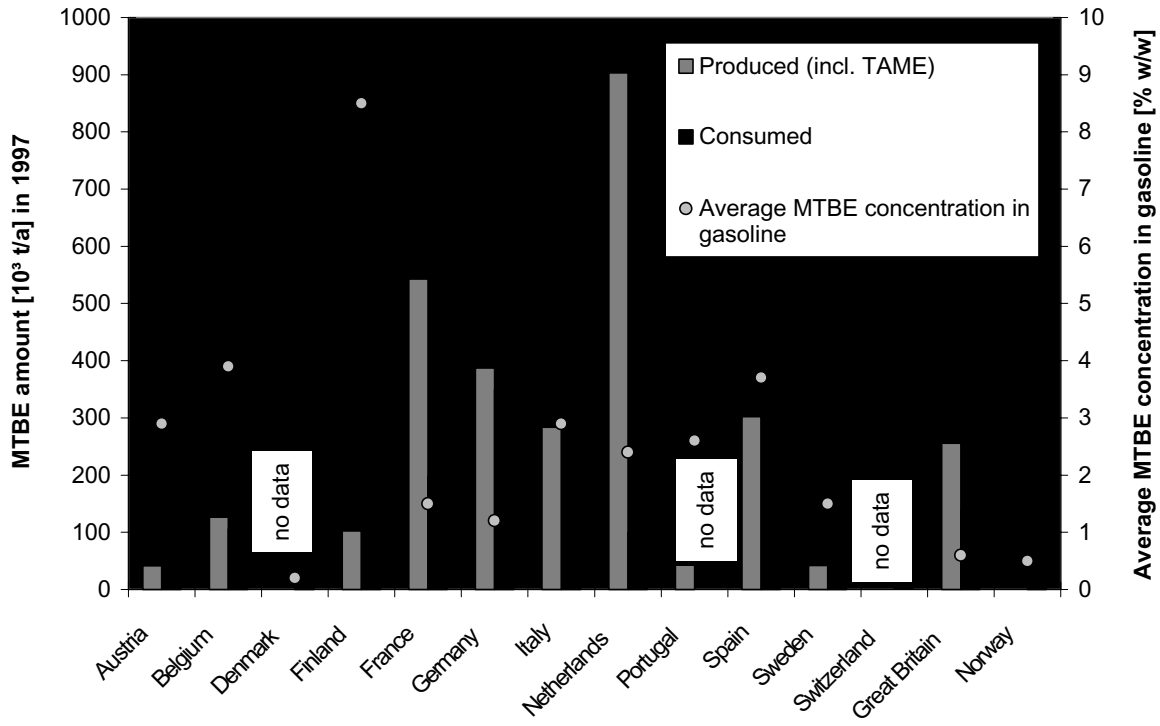


Figure 1-3 Amounts of methyl tert-butyl ether (MTBE) produced and consumed in European countries in 1997 [DEWITT COMPANY, 1998; MEF, 2001].

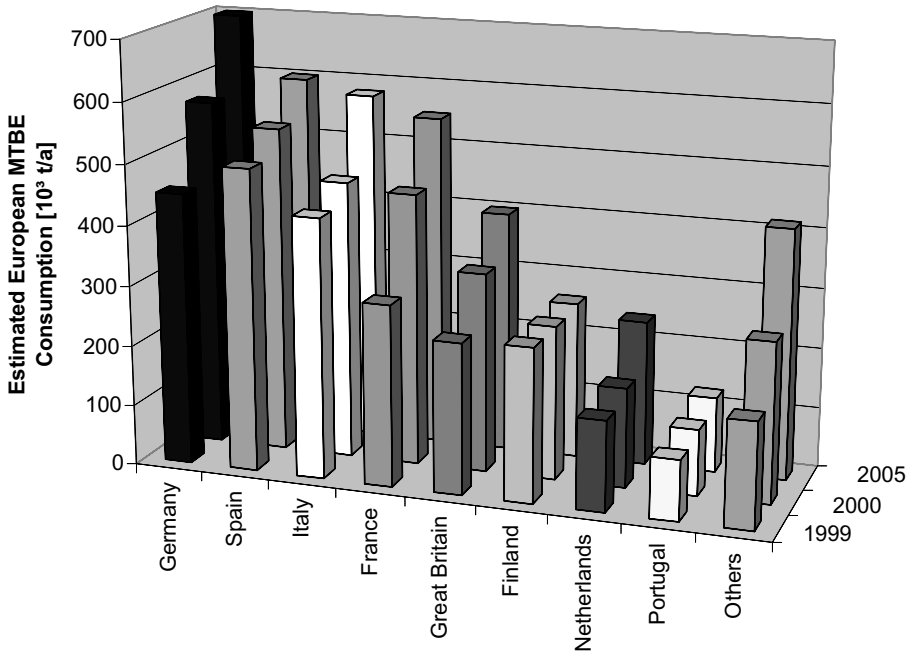


Figure 1-4 Estimated European consumption of methyl tert-butyl ether (MTBE) in the years 1999, 2000 and 2005 [DEWITT COMPANY, 1999].

MEF, 2001]. This assumption can be concluded from MTBE and ETBE amounts produced in France, where only one petroleum company exists, Elf-Total Petrofina. This company produces about 250,000 t/a of MTBE and about 250,000 t/a of ETBE [BEKRI, 2000]. The MTBE seems to be used essentially outside France, and the ETBE is introduced into the unleaded gasoline at low concentration (about 1 %). MTBE is also produced by foreign companies (Arco and others) in France which seems to be used also outside France.

MTBE is the dominant petrol oxygenate in the EU and it has been added to petrol blends since the mid 1970's, in the beginning at low levels (2 – 5 % (w/w)) to boost the octane rating of unleaded premium gasoline. More recently, it has been added at higher concentrations of 11 – 15 % (v/v) to promote more efficient combustion of petrol and improve air quality. Recently, MTBE has also been detected in groundwater in Denmark and as a result prices for super premium unleaded gasoline have been raised in order to reduce its consumption [WOLFF, 2000].

From 1995 to 1999, the consumption of MTBE in the EU has remarkably increased by 23 % and industry predicts a steady growth [DEWITT COMPANY, 1998]. For octane boost only, it represents a fairly expensive blending component and the company estimated an annual use

of about 4 mio t/a, among other blending substances, until the end of the year 2005. They believe that MTBE will play the major role in the necessary reduction of aromatics. An additional increase in MTBE amounts consumed due to new legislation from 2005 on remains difficult to estimate. However, it is assumed that until 2005 average European MTBE concentrations in gasoline will presumably be in the range of 1 – 4 % (v/v) [LITTLE, 2001] and about 4 mio t/a will be consumed until 2005 [MEF, 2001]. DEWITT COMPANY [1999] estimated an increase in the MTBE consumption by 48 % in Europe from 1999 to 2005.

Approximately 1.5 % of the MTBE amout consumed is used as a chemical to produce high purity isobutylene, as a solvent in the pharmaceutical industry and as a therapeutic agent for in vivo dissolution of cholesterol gallstones in humans [WHO, 1998].

In Europe, problems arising from an increased MTBE use in the future are evaluated differently. Generally, lower environmental MTBE concentrations compared to California are expected, because it is worth keeping tanks in good condition when the cost/ litre is around seven times higher than in the U.S.. If a tank leaks in Europe, it leaks products for which tax has already been paid. In the U.S., the fuels are taxed when being delivered to the petroleum stations. Other arguments were the existence of double-sided tanks in Germany, the more central organization of the water supply in Europe compared to the U.S. and that detections of oxygenates at traceable levels in groundwater has been a very isolated problem in Europe so far [WALKER, 1999]. The chairman of the European Association of Oxygenated Fuel Producers (H. Rovers) recently claimed that the way the MTBE issue is handled in the U.S. is mainly a result of strong political lobbying against MTBE and bad science. He does not believe that the U.S. has made a proper evaluation of the problem, and he trusts that such error will not be replicated in Europe. Although the toxicity, particularly MTBE's long-term carcinogenic activity is not yet fully understood, he compares MTBE to tea or talcum powder as all substances fall into the same category of toxicity [ROVERS, 2000]. Furthermore, he concluded that, in future, the need for gasoline and with it, the need for MTBE will decline. However, currently and in the near future, the MTBE demand is rising and will very likely even stronger increase [DEWITT COMPANY, 1998 AND 1999]. The view on the subject of the oil company Shell significantly differs from the former opinion. The MTBE problem is not simply evaluated and the company believes that a constructive dialogue is required between the key parties in order to determine the best way forward. The aim should be to ensure full understanding of the complexities of the issue and to seek practical solutions which balance

off possible risks, benefits and costs. Different solutions can result including that society might accept the groundwater risk or ubiquitously occurring MTBE concentrations associcated with the use of MTBE given that there are no health issues [ANONYMOUS, 2000C].

Detections of oxygenates in the environment were reported from Finland (TAME and MTBE), in tap water (ETBE) from France [LA VOIE DU NORD, 1999], in lake and groundwater in Denmark (MTBE), in urban/ rural air and Zürichsee from Switzerland [BUWAL, 1999; SCHMIDT, 2000], in groundwater from Austria, Netherlands, Sweden and Great Britain [EAUK, 2001; MEF, 2001].

1.1.3 Germany

In Germany, the use of the gasoline additive tetraethyl lead increased until 1972 and since then, it was partly substituted by increased concentrations of aromatic hydrocarbons, mainly benzene, toluene, ethylbenzene, xylenes, (BTEX) and trimethylbenzenes. The use of tetraethyl lead as gasoline additive damaged the catalysts of vehicles and resulted in measurable environmental concentrations of the compound. Since 1999, leaded gasoline was not sold anymore (Figure 1-5). But soon, the carcinogenic effect of benzene was not further acceptable for public health. Since the mid 1980‘s, MTBE has been added to gasoline in Germany as an octane booster. The average MTBE content in super premium unleaded gasoline of 7.7 % was reported from an investigation of gasoline in 1998 [BREUM, 1998]. In 1999, super premium unleaded gasoline, regular unleaded gasoline and the new „Optimax“ gasoline showed average MTBE contents of 9.8, 0.4 and 11.9 % (w/w), respectively. The values for Euro super unleaded gasoline varied from 0.4 to 4.2 % (w/w) [ACHTEN AND PÜTTMANN, 2001A]. Super premium unleaded gasoline (RON = 99) shows highest average MTBE concentrations but it is consumed to significantly lower amounts than Euro super unleaded (RON = 96) which is characterized by lower concentrations of MTBE (Figure 1-5). Both form the main part of the consumed amount of the ether. The use of regular unleaded gasoline (RON = 93) has slowly decreased since 1991. Instead, since 1990, the use of Euro super unleaded has increased significantly up to about $18{,}000*10^6$ t in 1999/ 2000. The average MTBE concentration in German gasoline is 1.2 – 1.71 % (w/w) [PAHLKE ET AL., 2000; MEF, 2001; SCHOLZ, 2001]. Different authors estimated the total MTBE use in Germany. PAHLKE ET AL. [2000] estimated the MTBE production capacities of German refineries and chemical industry to be

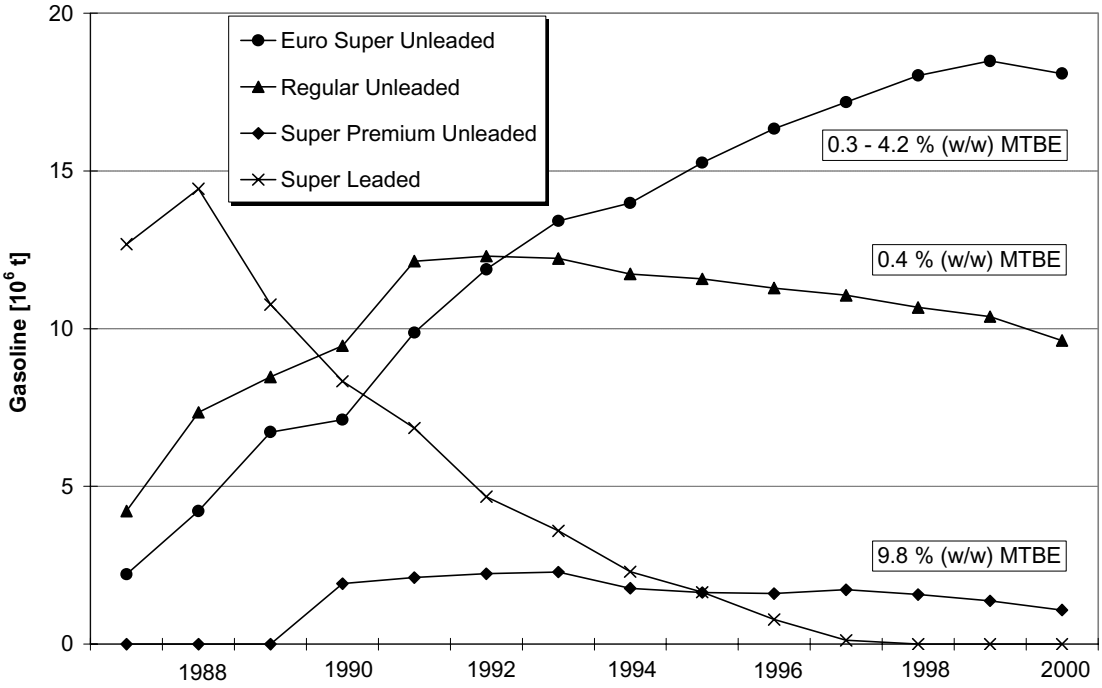


Figure 1-5 Development of the gasoline consumption of regular unleaded, Euro super unleaded, super premium unleaded and super leaded in Germany [STATISTISCHES BUNDESAMT, 2001] and average content of methyl tert-butyl ether (MTBE) in 1999 [ACHTEN AND PÜTTMANN, 2001A].

Table 1-1 Estimated production capacities of methyl tert-butyl ether (MTBE) [kt/a] of German refineries and chemical industry [PAHLKE ET AL., 2000].

	MTBE Capacity [kt/a]	
Refineries	**1995**	**1999**
DEA/ Heide	12	12
DEA/ Wesseling	60	63
PCK/ Schwedt	80	84
Mider/ Leuna	50	50
Bayernoil/ Ingolstadt	22	35
MIRO/ Karlsruhe	120	150
Mobil Oil/ Wörth/ R	42	0
No data from: Shell/ Hamburg; Shell/ Godorf; BETA/ Wilhelmshafen; HOLBORN/ Hamburg; Wintershall/ Lingen; RuhrOel/ Gelsenkirchen; Esso/ Ingolstadt and OMV/ Burghausen		
Chemical Industry		
Degussa Hüls, Marl	150	150
Total	**536**	**544**

approximately 550,000 t/a (Table 1-1) and the amount consumed to be roughly 500,000 t/a in 1999. The two refineries with the highest production capacities of 120,000 – 150,000 t/a are Degussa Hüls at Marl near the Lippe river and MIRO at Karlsruhe near the Rhine river. Others are situated at Schwedt, Wesseling/ Cologne, Leuna, Wörth/ R, Ingolstadt and Heide. The MTBE concentrations according to mean concentrations in different types of gasoline [CONCAWE, 1996; DGMK, 1994; BREUM, 1998] were calculated by the author. From the comparison of the data (Figure 1-6) it can be estimated, that in 1999, the total MTBE amount used in Germany is in the range of 450,000 to 500,000 t/a. A rapid increase in the use of the oxygenate can be concluded until 1993 from Figure 1-5 and 1-6. After a rather constant development of the annual consumed amounts until 1998, currently and in the future, an increase from 1999 to 2005 of 40 - 56 % is estimated [DEWITT COMPANY, 1999; ACHTEN AND PÜTTMANN, 2001A] which is comparable to theamout estimated for Europe of 48 %.

About 7,500 t were used for industrial purposes in 1999 [MEF, 2001].

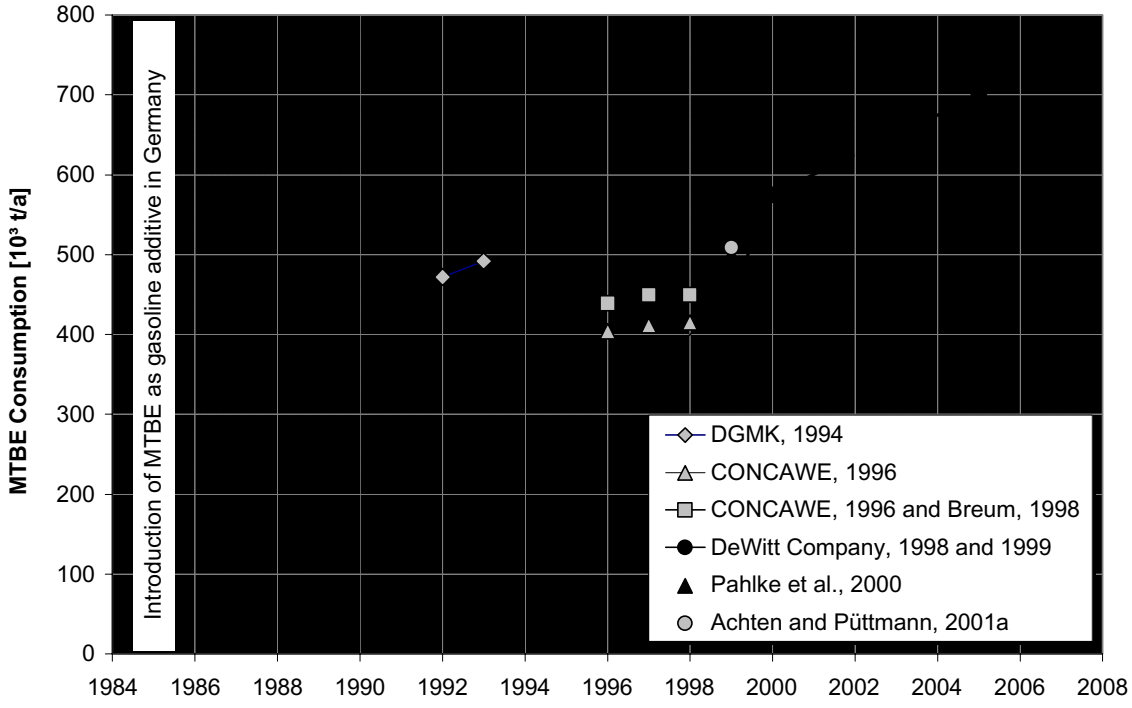


Figure 1-6 Estimated consumption of methyl tert-butyl ether (MTBE) in Germany according to different sources. Black symbols indicate total consumption and grey symbols show consumption as oxygenate only.

First analytical data of the oxygenate in the German environment were reported for surface water and precipitation in 1999 [ACHTEN AND PÜTTMANN, 2000 AND 2001B; BRAUCH ET AL., 2000A, PAHLKE ET AL., 2000; ACHTEN ET AL., 2001A, 2002A AND B], followed by observations in groundwater [Kolb, 2000; BRAUCH ET AL., 2000A; KLINGER ET AL., 2000; SCHIEDEK ET AL., 2000, BLW, 2000; EFFENBERGER ET AL., 2001, LUBW, 2001].

In Germany, authorities only recently began to evaluate the MTBE situation in the country [PAHLKE ET AL., 2000; PAHLKE, 2000] and decided not to implement a drinking water and surface water standard because MTBE concentrations in Germany are believed to be generally low. Other reasons for the decision were the presence of significantly lower MTBE concentrations in german gasoline compared to some U.S. states, decreasing MTBE emissions from automobiles and handling of MTBE by improved technology, such as use of double-sided tanks at gasoline stations from 1992 to 1998 due to an implemented directive. Very small fuel stations that sold less than 100,000 t/a were not covered by the directive, but they represent only a very small part of the overall gasoline pool. At the beginning of 1998, the remediation of 70 % of all petroleum stations was completed, covering more than 95 % of the stations that sell more than 5 mio t/a of gasoline [DEWITT COMPANY, 1999]. Additionally, the conclusion of the WORLD HEALTH ORGANIZATION in 1998 [WHO, 1998] that acute health risks for the public from the use of MTBE are unlikely and the reduction of emissions like benzene, CO and hydrocarbons were used as arguments for the use of MTBE. The Umweltbundesamt estimated a reduction of MTBE emissions in Germany from approximately 6000 t/a in 1992 to about 2200 t/a in 1999. However, monitoring of the oxygenate particularly at sites contaminated with gasoline has been intensified by the Umweltbundesamt [PAHLKE ET AL., 2000] because concentrations are generally higher at these sites.

The German government concluded that from the German MTBE use in gasoline, no acute health risks are known and are probably not expected in the future [PAHLKE ET AL., 2000].

1.2 Legal aspects

1.2.1 United States of America (U.S.)

The regulations on American exhaust emissions from vehicles were already described in chapter 1.1.1. In December 1997, the U.S. EPA's Office of Water issued a drinking water advisory for MTBE. It recommends a limit of 20 – 40 µg/L for drinking water as the range

that is sufficiently low enough to prevent human health risks and ensure no unpleasant odor or taste of the water. The EPA has not yet established a maximum contaminant level for MTBE in water and it is expected in 2006. More recently, the public health goal of 13 µg/L in drinking water based on cancer studies in rats and mice was proposed.[OEHHA, 1999].

Table 1-2 Aqueous cleanup levels for methyl tert-butyl ether (MTBE) in different U.S. States [Jacobs et al., 2001].

U.S. Cleanup Levels for Methyl *tert*-Butyl Ether (04/01/00)

10 µg/L	New York
13 µg/L primary (health effects)/ 5 µg/L secondary (taste and odor)	California
18 µg/L	Lousiana
20 µg/L	Alabama, Hawaii, Kansas, Oklahoma, Pennsylvania, Washington
20 µg/L/ 40 µg/L	Oregon
20 µg/L/ 200 µg/L	Nevada
20 µg/L drinking water/ site specific	Maryland
30 µg/L	Montana
35 µg/L	Arizona, Maine
40 µg/L	Minnesota, Ohio, South Carolina, Vermont
40 µg/L groundwater quality standard/ 20 µg/L preventative action level	Rhode Island
40 µg/L projected	Michigan
45 µg/L projected	Indiana
50 µg/L residential/ 500 µg/L industrial	Florida
55 µg/L	Mississippi
60 µg/L	Wisconsin
70 µg/L	New Hampshire, New Jersey
70 µg/L projected	Illinois
70 µg/L groundwater drinking supply/ 50 mg/L groundwater source for vapor emissions to buildings	Massachusetts
100 µg/L	Connecticut, New Mexico
180 µg/L	Delaware
200 µg/L, proposed at 70 µg/L	North Carolina
200 µg/L	Wyoming
200 µg/L action level	Utah
40 – 400 µg/L depending on use	Missouri
site specific	Arkansas, Colorado, Idaho, Virginia
waiting for EPA cleanup levels in 2006	Alaska, Georgia, Iowa, Kentucky, Nebraska, North and South Dakota, Tennessee, Texas, West Virginia

Clean-up levels for MTBE in water, mostly groundwater, differ from state to state (Table 1-2) and vary from 10 µg/L (New York) to 400 µg/L (Missouri). In California, a standard of 13 µg/L was implemented on the basis of health effects whereas a secondary standard of 5 µg/L ensures that the odor and taste of the ether in drinking water is not perceived. In the states of Oregon, Nevada, Maryland, Rhode Island, Florida and Massachusetts also two standards of different levels and in Arkansas, Colorado, Idaho and Virginia Site specific levels are used. In Missouri, the standard is depending on use and a group of 10 states is waiting for a standard proposed by the EPA in 2006.

In 1997, the EPA recommended a reference concentration for the air of 0.5 mg/m³ (Estimation of the daily concentration inhaled that does not represent any risks –except carcinogenic ones- to sensitive humans life-long) [TESSERAUX AND KOSS, 1999] which was revised to 3 mg/m³ after additional data on the effects on chronic exposures in late 1992 [DAVIS AND FARLAND, 2001]. At work (8 h mean), a standard of 144 mg/m³ was recommended by the AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS [ACGIH, 2001]. As it can be expected, the ban of MTBE proposed by the EPA has been criticized by the Oxygenated Fuel Association. Its director claimed the initiative a political move that will have disastrous effects on the environment and gasoline prices. If the EPA continued its course, it was inviting a legal challenge [ANONYMOUS, 2000B]. Recently, California Court has rejected a lawsuit against the MTBE ban by the producers of the oxygenate [ANONYMOUS, 2001B]. A resident in Florida has filed the first MTBE class action lawsuit hitting Exxon Mobil which is copied by people from other states [MARXSEN, 2001]. Anyway, the oil companies are already accused for conspiracy concerning the existing situation. They are accused to have purposely deceived public and government about the dangers of MTBE towards groundwater for profit reasons [BOLOGNA, 2000]. However, the oil companies reject the responsibility for the disaster and in turn make the government responsible because leakages of underground storage tanks were not controlled effectively by the state. Anyway, it is believed that most of the MTBE now showing up in California wells originally came from leaking underground storage tanks (LUSTs) long since either shut down or upgraded to prevent further leaking. In effect, it is stated that the California MTBE ban remedies a problem that has already been solved [MARXSEN, 2001]. MARXSEN also made the point that, clearly, it was only after MTBE was first reported to be a groundwater threat (in 1980) that it effectively mandated as a gasoline additive. Although the "Clean Air Act Amendments" do not call for MTBE as the oxygenate of choice, it was well known that it represented the compound commonly used. Recent progress towards banning it comes more from evolving political processes than from

new scientific discoveries [MARXSEN, 2001]. He concluded that the current effort to ban MTBE underscores how overzealous and wrong-headed enforcement of U.S. environmental regulations continues to damage the country's economy. Aspects of law concerning the MTBE dilemma and particularly underground storage tank regulations are summarized by [FAULK AND GRAY, 1999].

1.2.2 European Union (EU)

Until 1971, passenger car exhaust emissions were uncontrolled and in the following years, gradual control actions have been implemented. In 1991, as a consequence of the changes in legislation, the implementation of the Directive 91/441/EEC („EURO I") standards, it was necessary for all new petrol cars to be equipped with closed-loop three way catalyst and with carbon canisters for evaporative emission control. These technologies first entered widespread use in the EU from 1993 on. Emissions from gasoline distribution were regulated by the Directive 94/63/EC in 1994. The requirements of the directive limit the annual total loss of petrol during filling of storage tanks to 0.05 – 0.1 kg/t losses each from petrol in delivery depots, losses during filling and emptying of mobile tanks in delivery depots and during filling of the storage tanks at gas stations. During unloading from tank truck to station tank, vaporized petrol is collected and several stations are equipped with inlets that are attached to the petrol pistol for the reduction of emissions. Other directives (e.g. „EURO II) are aimed at the reduction of common exhaust emissions. Directive 98/70/EC („EURO III") regulates maximum content of MTBE as „ethers containing 5 or more carbon atoms per molecule" to 15 % (v/v). From 2000 on, new petrol quality standards were implemented that limited volatility and concentrations of several compounds of gasoline: Reid vapor pressure in summer (60 kPa), sulphur content (150 mg/kg), olefins (18 % (v/v)), aromatics (42 % (v/v)) and benzene (1 % (v/v)). Until 2005, the total concentration of aromatics will be restricted to 35 % (v/v) and the one of sulfur to 50 mg/kg. Lower octane numbers resulting from the reduction of aromatics will probably be compensated by higher MTBE concentrations in order to provide the quality of the gasoline. Recently, this has been evaluated as being acceptable for groundwater in the EU because the European Commission is not of the opinion that MTBE contaminations in groundwater is widespread across the Community [EC, 2001]. Toluene, the xylenes and trimethyl benzenes represent some of the major components of gasoline which indicates that the MTBE increase in gasoline in the future will probably be significant.

Sweden investigated health aspects of MTBE already in 1988 that led to an allowed concentration of 180 mg/m³ at work in Sweden and Finland since 1993 [TESSERAUX AND KOSS, 1999].

1.2.3 Germany

In Germany, only little data exist dealing with regulations on MTBE. The restrictions of gasoline handling were already desribed in chapter 1.1.3.
MTBE is classified to be easily flammable (F, R11) and irritating if it is contacted (Xi, R38). (Table 1-3). The security-phrases (s-phrases) advice

?? To keep the chemical away from children (2)
?? To keep the bottles close to ventilation (9)
?? To keep away from fire (16)
?? Not to breathe aerosols and vapor of the chemical (23)
?? Not to contact with skin (24)
?? Not to pour the chemical into the sink (29)
?? To ensure no electrostatic energy (33)

At a national scale, the risk of the oxygenate for water is expressed by assignment to „Wassergefährdungsklasse 1“ which reprents the category with lowest risks [KLOEPFER, 1999]. Recently, the maximum concentrations at work in Germany (MAK-Wert) was determined to be 50 mL/m³ (180 mg/m³) [SENATSKOMMISSION, 2000].
The county of Berlin prescribes a clean-up level of 100 µg/L [RIPPEN, 2001] and 15 µg/L has been suggested in Rheinland-Pfalz.

Table 1-3 Health and safety advices for methyl tert-butyl ether (MTBE) relevant for handling by humans.

Classification of MTBE	
Physico-chemical:	F
Health classification:	Xi
R-phrases:	R11; R38
S-phrases:	2-9-16-23-24-29-33

2 SYNTHESIS, PROPERTIES OF MTBE AND ITS BEHAVIOR IN THE ENVIRONMENT

2.1 Synthesis

The synthesis of MTBE, as commercially implemented, is achieved through the additon of methanol to isobutylene that is a cheap by-product in refineries. The reaction occurs in the presence of a sulfur-acidic catalyst (Ambelist, K2611) [DEGUSSA HÜLS-OXENO, 2001], which is necessary to form the reactive intermediate compound, the carbo-cation (Figure 1-7). The reaction is formally known as the electrophilic addition of methanol to isobutylene. There are two possible orientations of the molecule that can result from the reaction. The chemically preferred orientation is represented by MTBE. The tertiary structure is overwhelmingly

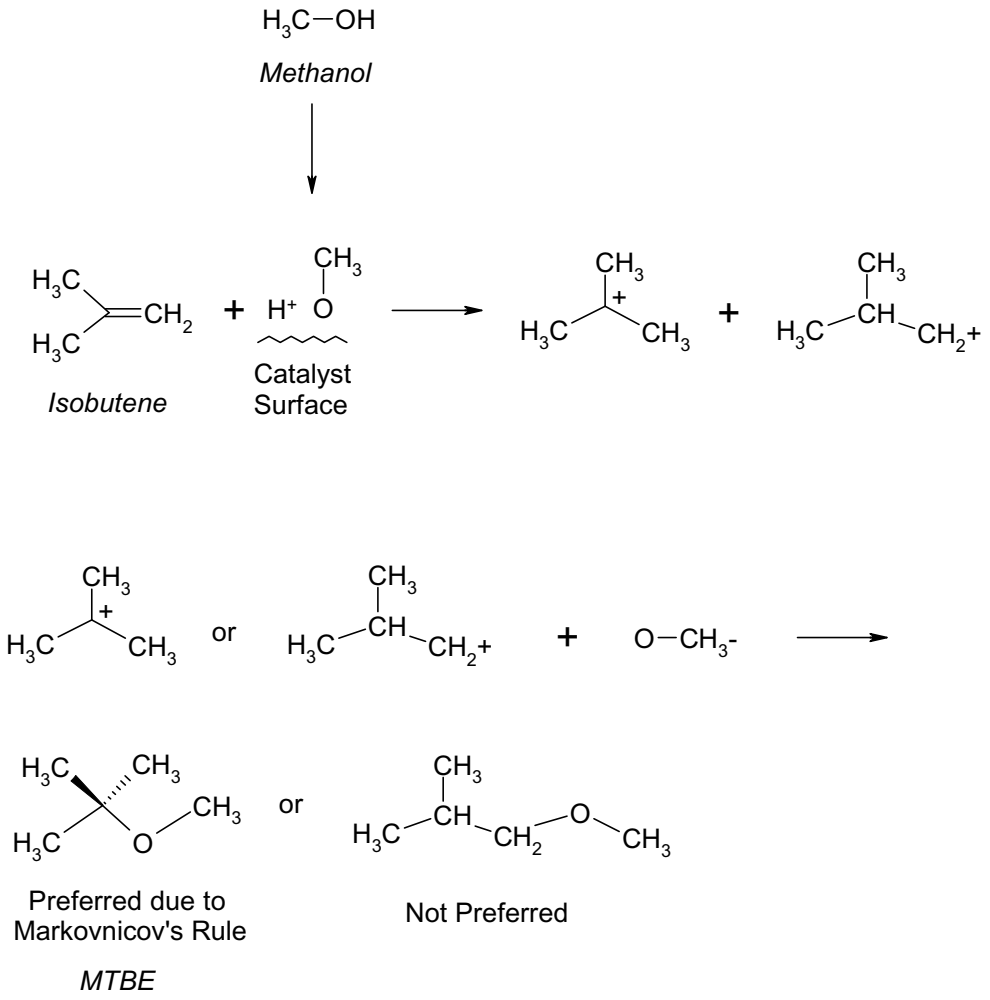


Figure 1-7 Synthesis of methyl tert-butyl ether(MTBE) by the additon of methanol to isobutylene [JACOBS ET AL., 2001].

preferred in the reaction pathway due to the stability to the tertiary carbocation.The preference of hydrocarbons to orient in the tertiary structure as a result of the formation of the most stable carbo-cation is known as Markovnikov's rule. It is the tendency of the inner structure of the hydrocarbons to conform the most stable orientation that produces the tertiary carbon structure. MTBE can also be prepared from methanol and tert-butyl alcohol.

2.2 Physico-Chemical Properties

Methyl *tert*-butyl ether or 2-methoxy 2-methyl propane (MTBE, CAS-No. 1634-04-4, EINECS-No. 216-653-1) is a chemically stable and colourless volatile liquid with an antiseptic odor. It is a polar molecule (the most polar constituent of gasoline) but compared to other ethers, it represents a relatively non-polar compound. Therefore, it is very water-soluble and soluble in most organic solvents. MTBE is flammable and combustible. It is characterized by a high research octane number (RON) of 117 and motor octane number (MON) of 102.

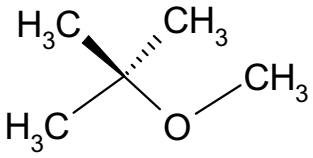


Figure 2-1 Structural formula of methyl tert-butyl ether (MTBE, $C_5H_{12}O$).

Unlike many ethers, MTBE does not tend to form peroxides during storage [MEF, 2001]. A molecular weight of 88.15 u of MTBE results from its structural formula that is shown in Figure 2-1. The structure is responsible for the resistance of the molecule to biodegradation and chemical oxidation. The presence of the oxygen atom in the molecule, as an ether linkage, provides a site for hydrogen bonding between water and MTBE. The energy of this bond is not high but is higher than the observed amounts for other molecules of environmental significance (e.g. chlorinated solvents). The amount of energy required to break this bond helps explain why the compound is difficult to air strip during remediation processing and separate from the aqueous solution. Impurities (<1.5 – 0.1 %) of methanol, 2-methylpropan-2-ol, 2,4,4-trimetylpentene, C_4-olefins, aromatics, C_{4-6} parafins, 2,4,4-trimethylpent-1-ene,

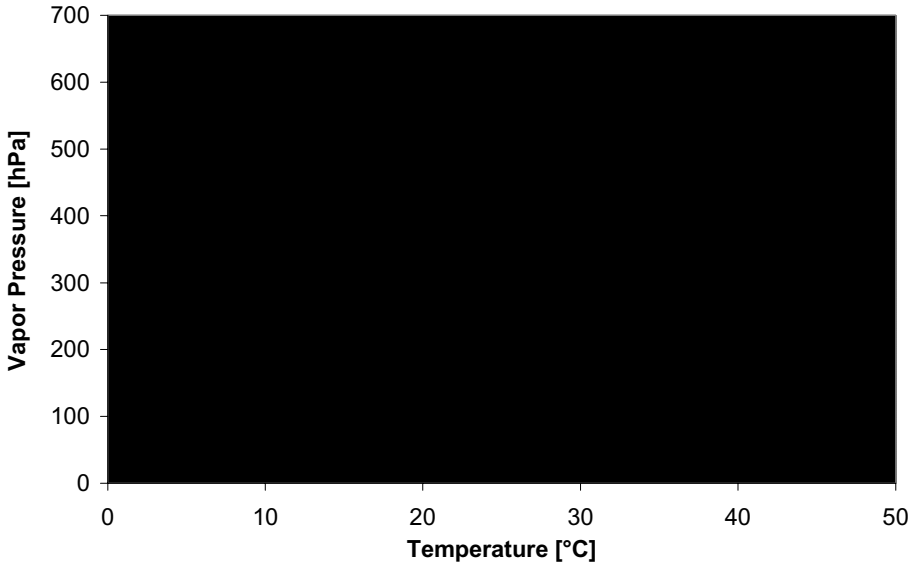


Figure 2-2 Temperature depending vapor pressure of methyl tert-butyl ether (MTBE) [MEF, 2001].

Table 2-1 Physico-chemical properties of methyl tert-butyl ether (MTBE).

Property	Value	Unit	Data temperature	Reference
Melting temperature	-108	°C	-	IUCLID, 1996
Boiling temperature	55.3	°C	-	IUCLID, 1996
Density	0.741	g/cm³	20 °C	IUCLID, 1996
Relative vapor density (air = 1)	3.04	-	-	AUERGESELLSCHAFT, 1989
Vapor pressure	270	hPa	20 °C	IUCLID, 1996
Surface tension	20	mN/m	20 °C	SCHOLZ ET AL., 1990
Water solubility	42	g/L	20 °C	STEPHENSON, 1992
Saturation concentration	970	g/m³	20 °C	AUERGESELLSCHAFT, 1989
Henry's Law coefficient	43.8	Pa*m³/mol	20 °C	ROBBINS ET AL:, 1993
	0.0169	-	20 °C	BAEHR ET AL., 1999
Log K_{OW}	1.06	-	25 °C	HUELS AG, 1989
Log K_{OC}	1.05	-	25 °C	SCHMIDT ET AL., 2001
Viscosity	0.36	mPa*s	-	SCHOLZ ET AL., 1990
Flash point	-28.2	°C	-	DAUBERT ET AL., 1989
Auto flammability	460	°C	-	ULLMANN'S, 1997

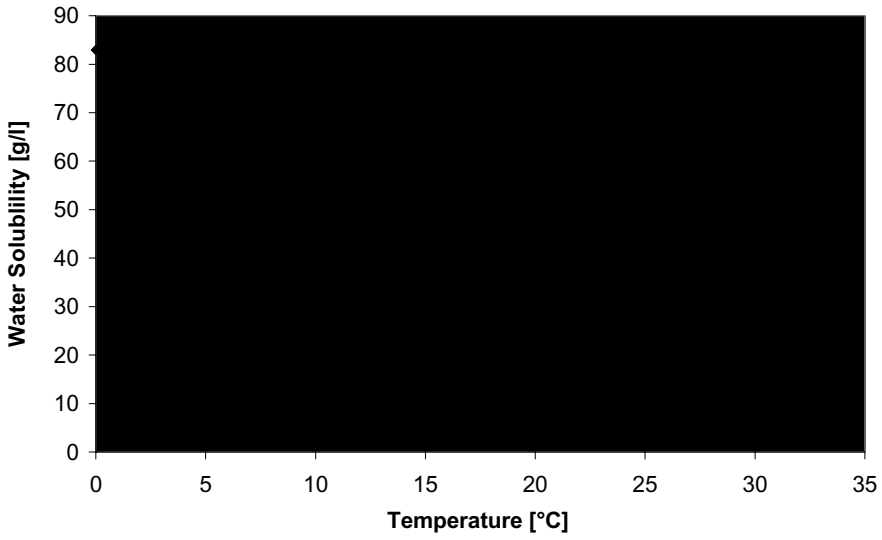


Figure 2-3 Temperature depending water solubility of methyl tert-butyl ether (MTBE) [MEF, 2001].

isobutene, di- isobutene (C_8H_{16} isomers), tri-isobutene ($C_{12}H_{24}$ isomers), tert-amyl methyl ether (TAME) and water were reported [MEF, 2001]. The physico-chemical properties of MTBE are summarized in Table 2-1. The significant volatility of the oxygenate is mostly the result of the low boiling temperature of 55 °C and the high vapor pressure (270 hPa at 20 °C) [IUCLID, 1996]. The vapor pressure of MTBE is about 3 times higher compared to benzene, an intensively investigated fuel compound. With an increase of 20 °C, the vapor pressure of MTBE roughly doubles (Figure 2-2). The high water solubility of the ether of 42 g/L (at 20 °C) [STEPHENSON ET AL., 1992] increases with decreasing temperatures (Figure 2-3) and, particularly, a rapid increase from 51 g/L at 10 °C up to 83 g/L at 0 °C is observed. This may play a major role for the environmental occurrence of MTBE. At 25 °C, the water solubility of MTBE is about 2.3 - 5 g/L from gasoline that is added 10 - 11 % (w/w) MTBE, whereas for nonoxygenated gasoline, the total hydrocarbon solubility in water is typically about 0.09 - 0.12 g/L [SQUILLACE ET AL., 1997A, HUTTUNEN, 1997]. The dimensionless Henry's Law coefficient for MTBE of 0.0169 (at 20 °C) [BAEHR ET AL., 1999] is low. The coefficient describes the partitioning of a substance between the air and water phase and a low value indicates that high amounts partition into the aqueous phase. The Henry's Law coefficient of MTBE increases with increasing temperatures (Figure 2-4) but at 25 °C (0.026) it is still about one order of a magnitude lower compared to benzene (0.23). Although it is a volatile

compound, it tends to partition into water at large amounts. Particularly, at low temperatures higher MTBE concentrations in the water phase compared to the air phase can be expected. The log K_{OW} for MTBE of 1.06 (at 25 °C) [HUELS AG, 1989] indicates that it does not significantly accumulate in organisms. The oxygenate only very weakly adsorbs to particles which is expressed by a log K_{OC} (1.05) and a retardation factor close to 1. The odor of MTBE is detected and recognized at average atmospheric concentrations in the range from 190 µg/m³ (0.053 ppm) to 290 µg/m³ (0.08 ppm). In water, the odor of MTBE is detected at an average concentration of 15 µg/L (2.5 – 190 µg/L). The average MTBE threshold of taste in water of 40 µg/L is higher and varies from 2.5 – 680 µg/L [KELLER ET AL., 1998]. Even if thresholds for taste and odors of 2.5 µg/L were reported, studies in the literature suggest that most persons would have higher thresholds [MEF, 2001].
The conversion factors of MTBE are temperature depending:

1 mL/m³ (ppm) = 3.94 mg/m³ or 1 mg/m³ = 0.254 mL/m³ (ppm) at 0 °C
[KOLB, 2001]
1 mL/m³ (ppm) = 3.66 mg/m³ or 1 mg/m³ = 0.273 mL/m³ (ppm) at 20 °C
[SENATSKOMMISSION, 2000]
1 mL/m³ (ppm) = 3.57 mg/m³ or 1 mg/m³ = 0.280 mL/m³ (ppm) at 25 °C
[MEF, 2001]

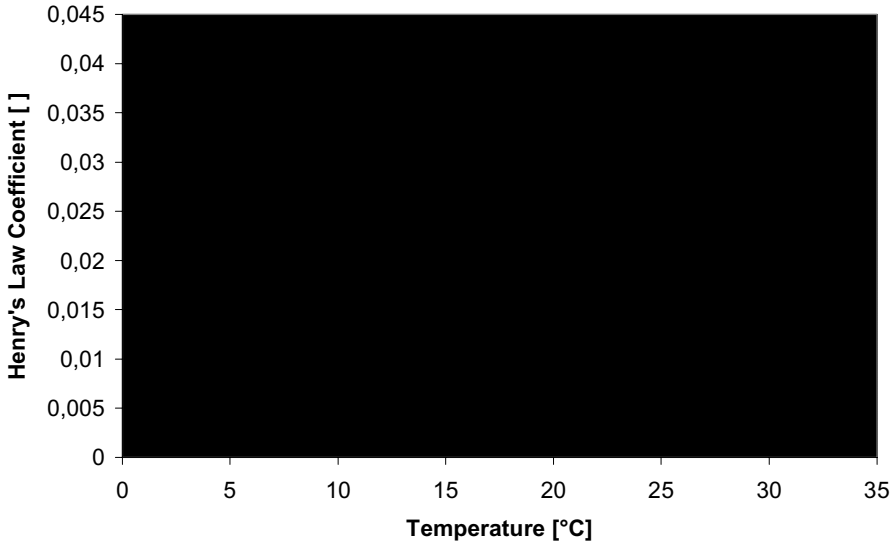


Figure 2-4 Temperature depending of Henry's Law coefficient of methyl tert-butyl ether (MTBE) [BAEHR ET AL., 1999].

2.3 Degradation

Generally, the *tertiary* structure, the ether bonding and the absence of long alkyl chains on the MTBE molecule makes it very resistant to biodegradation. The major limiting step to the oxygenate degradation is probably the accessibility and the cleavage of the ether bond. Assimilation of degradation products plays a subordinate role [KHAROUNE ET AL., 2001]. Two pathways for the initial transformation of MTBE have been proposed (Figure 2-5). Direct transformation of MTBE to *tert*-butyl alcohol (TBA) [STEFFAN ET AL., 1997] and transformation of MTBE to *tert*-butyl formate (TBF) [HARDISON ET AL., 1997], which subsequently undergoes abiotic or biotic hydrolysis to TBA, are the known degradation pathways. Abiotic hydrolysis of MTBE is a fast process with a half-life time of 5 days at neutral pH and a temperature of 22 °C [CHURCH ET AL., 1999]. After the initial transformation, the carbon of the methoxy methyl group and the carbon of the *tert*-butyl group may be further oxidized to CO_2 [STEFFAN ET AL., 1997]. Other degradation products are 2-propanol, acetone, formic acid, methyl acetate and formaldehyde [HOWARD ET AL., 1996; CHURCH ET AL., 1997].

2.3.1 Water and Soil

Generally, most studies indicate that MTBE in water or soil is difficult to biodegrade, particularly under anaerobic conditions [SUFLITA AND MORMILE, 1993; MORMILE ET AL., 1994; YEH AND NOVAK, 1994 AND 1995; HUBBARD ET AL., 1994]. The *tert*-methyl and ether groups on the MTBE molecule make it difficult to degrade in the subsurface. However, more recent investigations show the degradation of MTBE also under anaerobic [KANG ET AL., 1999], methanogenic [HURT AND WILSON, 1999], sulfate reducing [BRADLEY ET AL., 2001B], aerobic conditions [CHURCH ET AL., 1997; SALANITRO ET AL., 1994; SALANITRO ET AL., 1999; MO ET AL., 1997; SCHIRMER ET AL., 1998; HANSON ET AL., 1999; WILSON ET AL., 2001] and under different substrate conditions (MTBE alone, MTBE with diethyl ether, MTBE with DIPE, MTBE with ethanol and MTBE with BTEX) [PRUDEN ET AL., 2001]. Biodegradation occurred in the presence of a cosubstrate such as linear and branched short-chain alkanes or benzene under cometabolic conditions [STEFFAN ET AL., 1997; HARDISON ET AL., 1997; HYMAN ET AL., 1998; HYMAN AND O'REILLY, 1999; KOENIGSBERG ET AL., 1999] or with MTBE as sole carbon and energy source [SALANITRO ET AL., 1994; MO ET AL., 1997; HANSON ET AL., 1999; EWIES ET AL., 1997; PARK AND COWAN, 1997A AND 1997B; FORTIN AND DESHUSSES, 1998]. Cometabolic degradation of MTBE by a fungus has also been reported

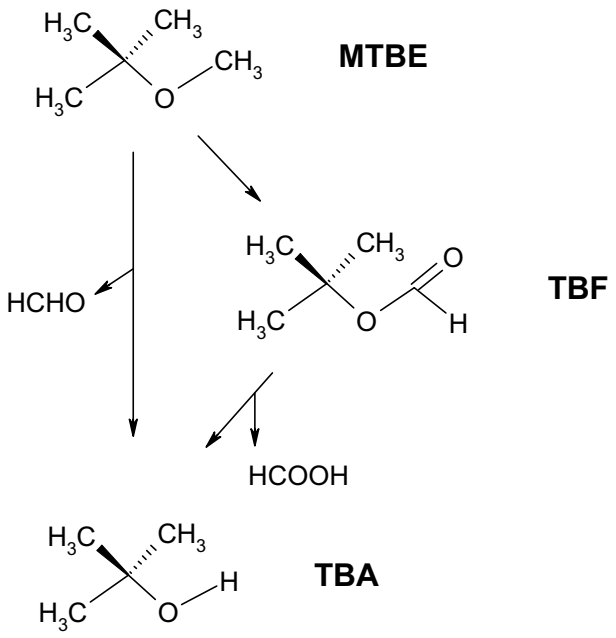


Figure 2-5 Proposed pathways for initial transformation of methyl-tert butyl ether (MTBE) to tert-butyl formate (TBF) and tert-butyl alcohol (TBA) [HUNKELER ET AL., 2001].

[HARDISON ET AL., 1997]. It is concluded that the presence of more easily biodegradable organics may inhibit MTBE biodegradation. Also, the cellular yield of microorganisms utilizing MTBE as sole organic carbon source can be expected to be very low, either because MTBE serves as a poor carbon and energy source, or because some of its metabolic intermediates can inhibit cellular growth [STOCKING ET AL., 1999]. Regardless of the specific aerobic mechanism, the presence of oxygen enhanced the biodegradation of MTBE [KOENIGSBERG ET AL., 1999; PARK AND COWAN, 1997B; YANG ET AL., 1998]. For significant MTBE degradation, oxygen levels need to exceed some threshold, apparently, above 2 mg/L. [STOCKING ET AL., 1999]. Recent laboratory studies have indicated that MTBE can be rapidly mineralized to CO_2 under oxic conditions by microorganisms indigenous to surfacewater bed sediments regardless of prior redox condition [BRADLEY ET AL., 1999] or previous MTBE exposure [BRADLEY ET AL., 2001A]. FINNERAN AND LOVLEY [2001] observed anaerobic degradation of MTBE in laboratory incubations of sediments from a petroleum-contaminated aquifer and in aquatic sediments. The addition of humic substances stimulated the degradation of MTBE in aquifer sediments in which Fe(III) was available as an electron acceptor. While biodegradation of MTBE has often been observed in laboratory experiments, there is less

evidence for it at field sites [BORDEN ET AL., 1997; SCHIRMER AND BARKER, 1998; BRADLEY ET AL., 1999; WILSON ET AL., 2000 AND 2002; LANDMEYER ET AL., 2001]. Different results have been reported for the degradation of TBA [SCHIRMER, 1999]. Hydrolysis and photolysis of MTBE in water will not be important removal processes [MEF, 2001]. MTBE is expected to have high mobility in soil and leaching with water is the predominant abiotic fate process in the subsurface. Recently, substrate interactions in BTEX and MTBE mixtures by an MTBE-degrading isolate was investigated [DEEB ET AL., 2001]. The observed severe inhibition of MTBE degradation by ethyl benzene and the xylenes and partial inhibition by benzene and toluene in the study suggest that the biodegradation of MTBE in subsurface environments would most likely be delayed until MTBE has migrated beyond the BTEX plume.

To the knowledge of the author, the degradation of MTBE during a riverbank passage and in surface water has not yet been investigated. In field studies, TBA and TBF have not yet been exactly identified as degradation products of MTBE.

2.3.2 Air

The reaction of MTBE in the atmosphere occurs essentially with OH-radicals only [TUAZON ET AL., 1991]. Reactions with radicals like $\cdot O_3$ and $NO_3\cdot$ are slow compared to the degradation rates achieved with OH-radicals [HOWARD, 1990; ATKINSON AND CARTER, 1984; WALLINGTON ET AL., 1986 AND 1987]. Photolysis of MTBE in the air can be neglected [CALVERT AND PITTS, 1966]. In the presence of NO_X in the atmosphere, the formation of TBF from MTBE was proposed by SMITH ET AL. [1991] by the following reactions:

$$(CH_3)_3C - O - CH_3 + \cdot OH \rightarrow (CH_3)_3C - O - (C\cdot)H_2 + H_2O$$

MTBE

$$(CH_3)_3C - O - (C\cdot)H_2 + O_2\ (+ NO) \rightarrow (CH_3)_3C - O - CH_2 - O\cdot\ (+ NO_2)$$

$$(CH_3)_3C - O - CH_2 - O\cdot + O_2 \rightarrow (CH_3)_3C - O - CHO + HO2\cdot$$

TBF

About 60 % of the OH-radical attack was observed at the methoxy group (O-CH_3) leading to the formation of TBA [JAPAR ET AL., 1990].
The degradation half-life time of MTBE is 3 - 6 days depending on environmental conditions (predominantly OH-radical concentration) [COX ET AL., 1982; TUAZON ET AL., 1991; SMITH ET AL., 1991; JAPAR ET AL., 1990, WALLINGTON ET AL., 1988]. A mean half-life time of 5.65 d was estimated by the MEF [2001] using a degradation constant of $2.84*10^{-12}$ cm/ molecule s^{-1} and it was concluded that atmospheric MTBE can be transported over long distances, e.g. thoughout Europe [SCHOLZ, 2001]. Atmospheric TBA is degraded at a rate constant (reaction with OH-radicals) of $7.37*10^{-13}$ cm/ molecule s^{-1} [SMITH ET AL., 1991].
Degradation products include *tert*-butyl formate (62 %), formaldehyde (40 %), methyl acetate (17 %), acetone (down to 2 %) and minor amounts of *tert*-butyl alcohol and acetaldehyde. Recently, the degradation of MTBE vapors by cometabolism with pentane has been observed [DUPASQUIER ET AL., 2002].

MTBE degradation in water and air is summarized by STOCKING ET AL., [1999], SCHIRMER, 1999, MEF [2001], and PRINCE [2000]. Remediation techniques suitable for the MTBE removal are discussed by STOCKING ET AL. [1999], DERNBACH [2000] and JACOBS ET AL. [2001].

2.4 Toxicity

Since the beginning of the MTBE use as oxygenate in gasoline in the United States, acute health system complains, such as headaches, nausea, dizziness, and breathing difficulties have been reported nationwide in the U.S. [JACOBS ET AL, 2001] . The toxicity of MTBE has not yet been finally evaluated. So far, the U.S. EPA [SQUILLACE ET AL., 1997A], the WORLD HEALTH ORGANIZATION [WHO, 1998], the EUROPEAN CENTRE FOR ECOTOXICITY AND TOXICITY OF CHEMICALS (ECOTOC) [EFOA, 2002] and the MINISTRY OF THE ENVIRONMENT FINNLAND [MEF, 2001] concluded that it appears unlikely that MTBE alone induces acute health effects in the general population under common exposure conditions. However, the EPA has classified MTBE as a possible human carcinogen [EPA, 2001].
Long-term exposure and toxicological effects with other pollutants present in the environment are unknown. Since the initial metabolic step of MTBE releases formaldehyde and *tert*-butyl alcohol (TBA), both of which are of toxicological interest, the relevant toxicokinetic features of the two metabolites need to be addressed as well.

Calculated and tested bioconcentration factors of MTBE vary from 1.4 – 2.7 which indicate low potential for bioconcentration [MEF, 2001]. MTBE exhibits low acute toxicity via oral, dermal and inhalation in humans and test animals. The case data from gall bladder removal patients show that the principal effects of MTBE are on central nervous system, including sedation, nausea and vomiting. The LD_{50} in rats varies from 2900 – 4800 mg/kg [MASTRI ET AL., 1969]; and the average is 4,000 mg/kg [MEF, 2001] for oral acute toxicity. The dermal LD_{50} is over 10,000 mg/kg and by inhalation, an LC_{50} from 79 – 139 mg/L [MASTRI ET AL., 1969; ARCO, 1980] with an average of approximately 100 mg/L [MEF, 2001] has been determined. MTBE can be considered a skin irritant but at low air concentrations, studies in human volunteers have shown no signs of eye irritation. The results from the study in mouse or the experience in human volunteers do not give reason to classify MTBE as respiratory irritant. Based on the available information, MTBE cannot be considered a mutagen. MTBE produces tumours in mice and rats at doses $\geq$ 11,000 mg/m³ [BIRD ET AL., 1997; MEF, 2001] after inhalation exposure. Tumours have been reported in rats at oral doses $\geq$ 250 mg/kg [BELPOGGI ET AL., 1995]. There is no evidence of a direct genotoxic mode of action. There are indications of carcinogenicity in two species.The tumours appear mostly at very high doses, and MTBE is not genotoxic in vitro or in vivo. On the other hand, the human relevance of the tumors observed cannot be neglected. MTBE does not cause significant toxicity to reproduction in rats. Based on the available data, MTBE is not considered to be toxic to foetal development [MEF, 2001]. For the determination of the maximum MTBE concentration allowed for workers in Germany, the cancerogenity and mutagenity of MTBE were assigned to the categories 3 B and group C, respectively [SENATSKOMMISSION, 2000]. These categories imply that more research is needed for a final evaluation. The Health Authorities of the city of Hamburg, Germany, concluded that relations between MTBE use and the occurrence of cancer have not been observed and it has been used for medical purposes for approximately 20 years [TESSERAUX AND KOSS, 1999].

It does not appear that the concentrations of MTBE in ambient water are toxic to aquatic organisms except during spills. Although there are no data on the terrestrial toxicity of MTBE, this appears not to be of concern since concentrations in ambient air are low and its half-life time is relatively short [WHO, 1998]. The SCIENTIFIC COMMITTEE ON TOXICITY, ECOTOXICITY AND THE ENVIRONMENT OF THE EUROPEAN COMMISSION [CSTEE, 2001] concluded that, in spite of its relatively low toxicity, MTBE is a chemical of concern due to its high production volume and relatively high persistence. MEHLMANN [2000 and 2001] drew attention to the possible misclassification of MTBE concerning its carcinogenic activity. In

1998, at a U.S. meeting of the NATIONAL TOXICOLOGY PROGRAM'S (NTP) BOARD OF SCIENTIFIC COUNSELORS, data were presented showing that exposure of MTBE caused carcinogenic effects in mice. Despite this evidence, the NTP Board defeated a motion to list MTBE as „reasonably anticipated to be a human carcinogen" by a vote of 6 to 5. Good public health policy dictates that the Board conducts another review of MTBE with proper consideration of the criteria that have been established for listing agents as carcinogens. A detailed summary of the toxicity of MTBE and TBA is given as part of the risk assessment of MTBE performed by the MINISTRY OF THE ENVIRONMENT FINLAND [MEF, 2001]. They concluded that as far as human health is concerned, risks for consumers are not expected and risk reduction measure already being applied are considered sufficient.
A recent study indicate that ambient MTBE concentrations documented in U.S. surface waters to date do not constitute a risk to aquatic organisms [MANCINI ET AL., 2002]
Toxicological data of other oxygenates like ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME) and di-isopropyl ether (DIPE) are insufficient.

2.5 Emission Pathways into the Aquatic Environment

Detectable MTBE concentrations in the aquatic environment can result from different emission pathways (Figure 2-4). There are point and non-point sources of the oxygenate affecting surface- and groundwater quality. Point source emissions like spills of MTBE into soil evaporate into air and solve into precipitation or can be transported without significant retardation into groundwater. As most MTBE is used as oxygenate, the main contributors of MTBE releases into the subsurface environment of soil and groundwater are leakage from underground storage tanks (LUSTs), pipelines, and spills at refueling facilities. High MTBE concentrations up to the mg/L range can be emitted from these point-source emissions into groundwater. They are not subject of this study and more information about MTBE in groundwater is summarized elsewhere [PAHLKE ET AL., 2000; SCHOLZ, 2001; BRAUCH ET AL., 2000A; MEF, 2001]. The gasoline component has also been detected in heating oil and diesel fuel up to 60 mg/L [ROBBINS ET AL., 1999; CUMMINS ET AL., 2001]. The occurrence of MTBE in the atmosphere is primarily a result of evaporative emissions and incomplete combustion (e.g. from highways, gasoline stations, parking garages, refineries, or chemical industry) [SQUILLACE ET AL., 1997A]. It is generally removed from the atmosphere by chemical degradation or by transfer into the aquatic environment via precipiation. Particularly in urban areas, precipitation falls onto roads or sealed areas close to vehicle traffic (e.g. ditches) where

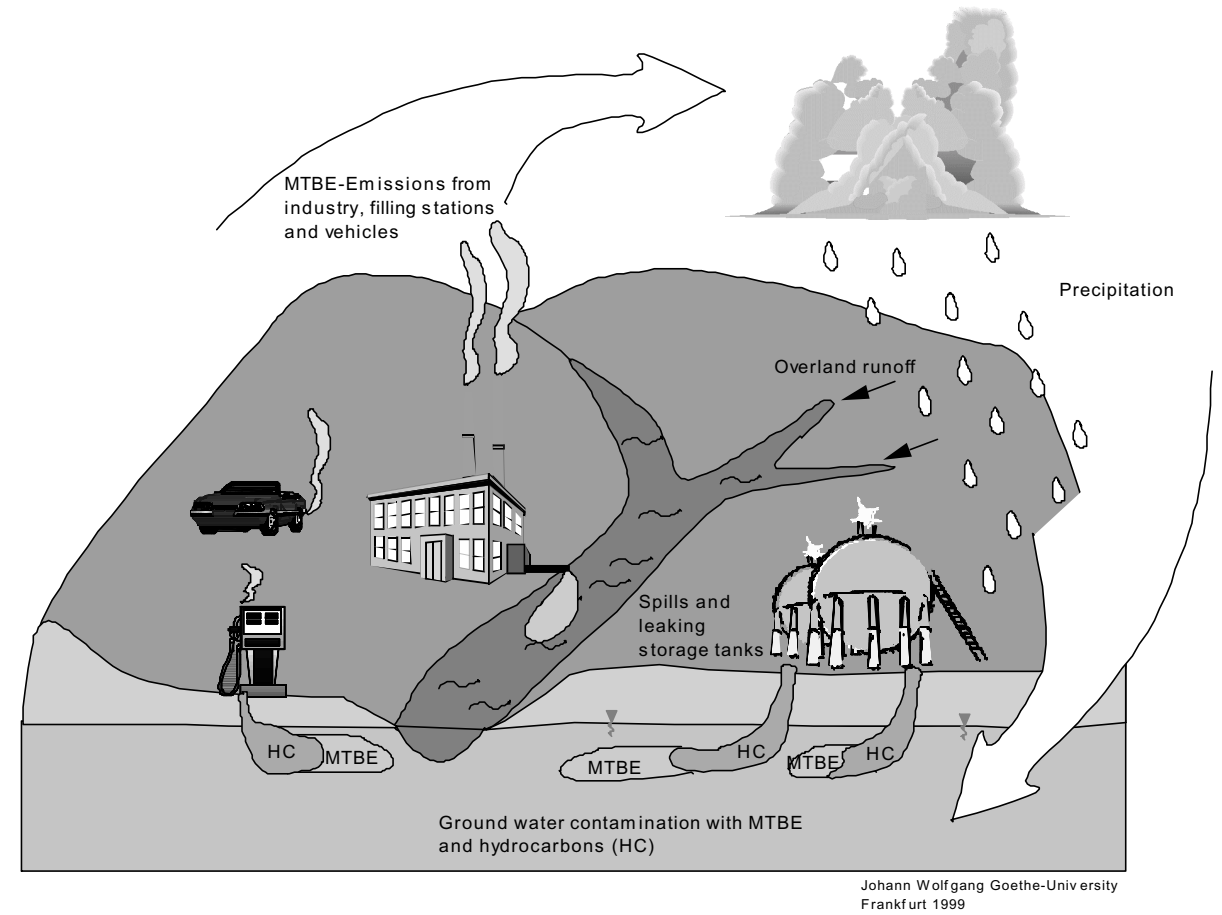


Figure 2-4 Emission pathways of methyl tert-butyl ether (MTBE) into the environment.

it is enriched in MTBE due to vehicle emissions (e.g. incomplete combustion, leakage from engines). Urban runoff is collected by culverts, concrete pipes, lined ditches or channels and is transported to sewage plants where it is mixed by industrial effluents containing MTBE. After the reduction of aqueous MTBE concentrations in the sewage plants mainly due to evaporation (43.1 %) [MEF, 2001], it is released (56.8 %) [MEF, 2001] into river water. Finally, direct emissions into river and lake water from motor water craft (e.g. jet skis, two-stroke engines) [REUTER ET AL., 1998; GABELE AND PYLE, 2000], spills from ships transporting and refuelling oxygenated gasoline and effluents from chemical industry also contribute to the MTBE load in surface water. Groundwater contaminated with MTBE dewatering into rivers represents an additional emission source but it has not yet been investigated. The oxygenate is frequently detected in the aquatic environment because large amounts of water can be contaminated: 1 mL of oxygenated gasoline containing 10 % of MTBE mixed with 4000 L of water will yield 20 µg/L of MTBE in water [SQUILLACE ET AL, 1997].

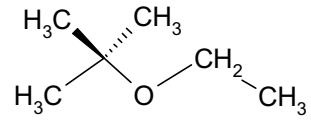
2.6 Behavior in the Environment

MTBE tends to partition strongly from the gas phase into the water phase if contaminated air is brought into contact with uncontaminated water. Hence, atmospheric emissions of the ether partition into atmospheric water, including precipitation. However, washout of gas-phase MTBE by precipitation would not, by itself, greatly alter the gas-phase concentration of the compound in air; 2.5 cm of precipitation will remove less than 0.5 % of the MTBE in the air (at 20 °C) [ZOGORSKI ET AL., 1997] The partitioning of MTBE to precipitation is nevertheless strong enough to allow for up to 3 µg/L or more inputs of the ether to surface and groundwater (at 10 % MTBE use in gasoline) [SQUILLACE ET AL., 1996]. The low value for the dimensionless Henry's Law constant indicates that once MTBE is solved into water, it tends to stay in the aqueous phase and is difficult to remove by aeration. Even at very small oxygenated gasoline spills into the subsurface (e.g. from gasoline containing 10 % of MTBE in the tank of a single overturned automobile) [JOHNSON ET AL., 2000], MTBE plumes in groundwater can reach kilometers of lenghts in comparison to benzene plume lengths of tens to hundreds of meters. High water solubility, practically no adsorption to subsurface solids and very poor degradability of MTBE are responsible for this behavior. In rivers, travel distances of MTBE for half-life times range from 0.8 km for shallow and fast moving streams to more than 900 km for deep and slow moving rivers [PANKOW ET AL., 1996]. In deep and

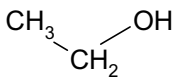
slow moving flows, MTBE volatilizes at rates similar to those for the BTEX compounds. In shallow and fast moving flows, it volatilizes at rates that are significantly lower than those for BTEX. MTBE does not concentrate in water or air but under non-equilibrium conditions, as mostly occur in the natural environment, it will move between air and water, leading to increasing or decreasing concentrations of the oxygenate in the compartments until equilibrium is established. The behavior and fate of MTBE in the environment is summarized by SQUILLACE ET AL. [1997A].

2.7 Comparison to Other Oxygenates

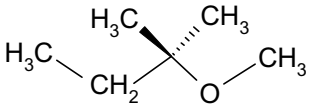
From the compounds that are classified into the group of oxygenates, MTBE is most important. However, there are few others and some of them are used in other countries. The second most-used fuel oxygenate is ethanol. The commercial use of the others including ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), methanol and di-isopropyl ether



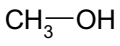
Ethyl tert-butyl ether (ETBE)



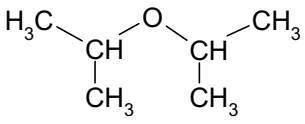
Ethanol



Tert-amyl methyl ether (TAME)



Methanol



Di-isopropyl ether (DIPE)

Figure 2-5 Stuctures of the oxygenates ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), di-isopropyl ether (DIPE), ethanol and methanol.

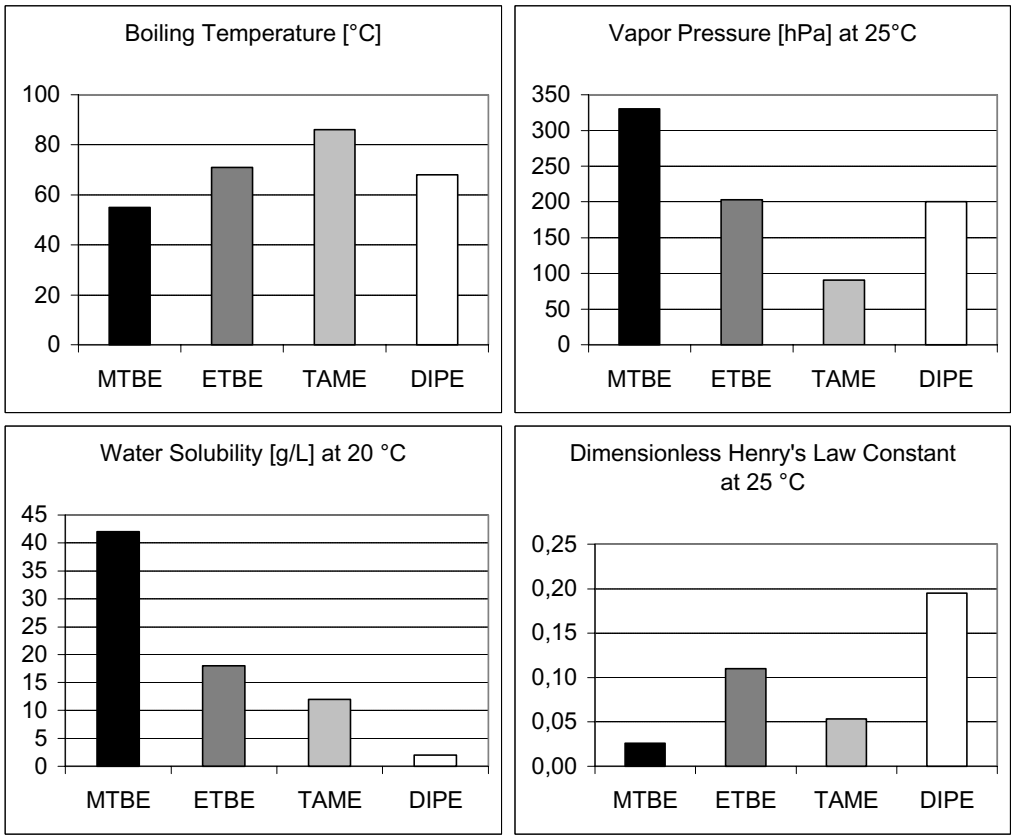


Figure 2-6 Comparsion of boiling temperature, vapor pressure, water solubility and dimensionless Henry's Law constant of the oxygenates ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), di-isopropyl ether(DIPE) to methyl tert-butyl ether (MTBE).

(DIPE) is very limited [ZOGORSKI ET AL., 1997]. The structures of the compounds are presented in Figure 2-5. Information on the behavior of other alkyl ether oxygenates is limited. ETBE and TAME can be expected to be also badly biodegradable, like MTBE, as both alkyl ethers are based on *tert*-carbon structures. The degradability of DIPE is unknown. Boiling temperatures, vapor pressures, water solubilities and the dimensionless Henry's Law constants of MTBE, ETBE, TAME and DIPE are compared in Figure 2-6. The water solubilities of 18 g/L for ETBE and 12 g/L for TAME are also high, although, compared to MTBE, they are lower by a factor of about two. The water solubility of DIPE of 2 g/L is lower than that of MTBE by a factor of 21. Therefore, the retardation factors particularly for ETBE and TAME can expected to be also very low. If the boiling temperatures and vapor pressures of the alkyl ethers are compared, the ranking from more volatile to less volatile compounds is MTBE ✍ ETBE, DIPE ✍ TAME. In the vicinity of Finish petroleum stations,

Table 2-2 Properties of the oxygenates ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), di-isopropyl ether (DIPE), ethanol, methanol, and tert-butyl alcohol in comparison to methyl tert-butyl ether (MTBE), benzene, toluene and para-xylene [SCHMIDT, ET AL., 2001; JACOBS ET AL., 2001; RIPPEN 2001; FITA, 1997; JOHNSON ET AL., 2000].

	CAS No.	Mol. Weight	MON[a]	Boiling Temp.	Density	Vapor Pressure	Water Solubility		Henry's Law Constant	Henry's Law Constant	Log K_{OW}	Log K_{OC}	Degra-dation
							pure	from RFG[b]					
		[u]	[ ]	[°C]	[g/cm³]	[hPa] at 25 °C	[mg/L] at 20°C	[mg/L] at 20°C	[ ] at 25 °C	[atm*m³*mol^{-1}] at 25 °C	[ ]	[ ]	
MTBE	1634-04-4	88	102	55	0.74	330	42 000	4 700	2.59E-02	6.40E-04	1.06	1.05	--
ETBE	637-92-3	102	102	71	0.74	203	18 000	1 300	1.10E-01	2.70E-03	1.74	0.95	-
TAME	994-05-08	102	112	86	0.76	91	12 000	1 400	5.32E-02	1.30E-03	1.55	1.28	-
DIPE	108-20-3	102	-	68	0.72	200	2 000	1 200	1.95E-01	4.77E-03	1.52	1.13	-
Ethanol	64-17-5	46	102	78	0.79	79	infinite	-	2.10E-04	5.20E-06	-0.31	0.2	++
Methanol	67-66-1	32	105	65	0.79	168	infinite	-	1.88E-04	4.60E-06	-0.77	0.44	++
TBA	75-65-0	74	100	83	0.79	56	infinite	-	5.73E-04	1.4E-05	0.35	1.57	-
Benzene	71-43-2	78	115	80	0.88	101	1760[c]	18[d]	0.23	-	2.12	1.92	-
Toluene	108-83-3	92	104	111	0.89	3 786	550[c]	25[d]	0.24	-	2.73	2.48	+
***p*-Xylene**	106-12-3	106	-	137	0.86	1 160	180[c]	20[d]	0.29	-	3.15	1.40-2.52	-

[a]Motor octane number, [b]Reformulated gasoline, [c]at 20 - 30 °C, [d]from conventional gasoline containing 1% benzene, 5% toluene, 10% xylenes

TAME (8.5 % in gasoline) concentrations in the air were reported to be lower by a factor of about 1.5 – 2 compared to atmospheric MTBE (2.7 % in gasoline) concentrations [VAINIOTALO ET AL., 1999]. Generally, TAME is characterized by volatilization possibly less than MTBE at a factor of about five, leading to lower environmental TAME concentrations. From the boiling temperatures and vapor pressures of ETBE and DIPE it could be concluded that both volatilize less than MTBE at a factor of may be 2.5. The dimensionsless Henry's Law constants of the alkyl ethers show a ranking of the preferred partitioning into water (compared to air) of MTBE ✍ TAME ✍ ETBE ✍ DIPE. From the comparison of the ethers, it can be concluded that MTBE shows the most unfavorable properties for the environment al impact compared to the others. However, if all alkyl ether were used at the same amounts in gasoline, the environmental concentrations of ETBE, TAME and DIPE were lower compared to MTBE, but not significantly. The expected half-life times of the alkyl ethers in air are similar to MTBE [ZOGORSKI ET AL., 1997]. The properties of the oxygenates are shown in Table 2-2.

Ethanol is the favorite oxygenate that will probably substitute MTBE in the future, at least in the U.S.. Unfortunately, the hygroscopic nature of ethanol-blended gasoline prevents its preparation at the refineries and distribution by pipelines. Distribution terminal receive gasoline and ethanol separately and both are mixed when they are pumped into a tanker truck for the delivery. Ethanol is, somewhat, comparable to MTBE. It is very good water and gasoline soluble, has a very low tendency to adsorb to mineral surfaces or volatilize from the aqueous phase. The main difference between both organics is ethanol's high degree of biodegradabilty under aerobic and anaerobic conditions. However, it can create a cosolvent effect, and the biodegradation of the „microbial candy" can deplete the groundwater of nutrients and electron acceptors necessary for the degradation of other gasoline components that are less attractive to microorganisms like the carcinogenic benzene. Downstream of spills, the cosolvent effect of ethanol could lead to very high concentrations of the alcohol in groundwater and a much more significant - possibly an order of a magnitude- increase in concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX). The impact of ethanol on more hydrophobic gasoline components is not known at this time. Ethanol is well degraded both, under aerobic and unaerobic conditions without any known toxic degradation by-products, although it seems difficult to ensure this for degradation products of other mechanisms induced by the presence of the alcohol. As the degradation requires a high oxygen demand, ethanol is likely to be degraded mainly und anaerobic conditions [POWERS ET

AL., 2001]. The results of various modelings of spills of ethanol blended gasoline indicate that benzene will cover longest travel distances in a plume. Gasoline with ethanol also raised some air quality concerns because incomplete combustion of the alcohol produces acetaldehyde, a hazardous air pollutant [HOGUE, 2000]. An amount of only 2 % (w/w) of ethanol in gasoline compared to fuel containing 5 % (v/v) of MTBE can increase acetaldehyde concentrations in the emissions by 80 – 100 %, part of which undergoes photochemical reactions in the atmosphere to make peroxyacetyl nitrate (PAN). On the other hand, decreases of 16 % in CO and 28 % in formaldehyde emissions also resulted from the ethanol use compared to the MTBE use [SCHIFTER ET AL., 2001].
An increased use of *tert*-butyl alcohol as oxygenate is not favorable as it is a known human carcinogen [CIRVELLO ET AL., 1995].

The relative trends favor ethanol and not MTBE when considering risks associated with oxygenated gasoline spills. The use of ethanol seems to lead to less problems but more research is needed.

3 ANALYTICAL METHODS

3.1 Method for Determination of MTBE in Gasoline by Gas Chromatography (GC)

3.1.1 Abstract

A simple method for the determination of methyl *tert.*-butyl ether (MTBE) in gasoline has been developed. The separation of MTBE from other analytes was controlled by the use of gas chromatography-mass spectrometry (GC-MS) in the full scan mode using the characteristic primary, secondary and tertiary ions *m/z* 73, 57 and 43. The mass spectrum did not show any superimposition of other analytes. The separation from the common gasoline component 2-methylpentane was sufficient for reliable quantitation. An application of the developed conditions using gas chromatography (GC) equipped with a flame ionization detector (FID) was performed by the analysis of regular, Euro super, super premium unleaded and „Optimax“ gasoline from petrol stations in the area of Frankfurt/M. Regular unleaded gasoline shows an average MTBE content of 0.4 % (w/w) whereas the MTBE content in Euro super varies between 0.4 and 4.2 % (w/w). The blending of MTBE to super premium has increased from 8.2 % (w/w) in 1998 to 9.8 % (w/w) on average in 1999. The recently introduced gasoline „Optimax“ shows an average MTBE content of 11.9 % (w/w). The presented method might also be used for the analysis of other ethers, such as ethyl *tert*-butyl ether (ETBE), which requires the use of another internal standard.

3.1.2 Introduction

In Germany little information has been published about the use of MTBE in gasoline so far. The methods used in order to analyse oxygenates in gasoline generally are complex. Among the methods used are gas chromatography (GC) [ASTM, 1989; DISANZO, 1990], gas chromatography-mass spectrometry (GC-MS) [HARDMAN ET AL., 1993; KANAI ET AL., 1994], high pressure liquid chromatography (HPLC) [PAULS, 1985], nuclear magnetic resonance (NMR) spectroscopy [MEUSINGER, 1999; SKLOSS ET AL., 1994], fourier transform infrared (FTIR) spectroscopy [IOB ET AL., 1998; CHOQUETTE ET AL., 1996; FODOR ET AL., 1996] and total oxygen measurement [FODOR ET AL., 1996]. The GC methods require single, dual or multicolumn column switching and/or back-flushing systems, extraction of the oxygenates

either with water or ethylene glycol or previous cleanup by acetonitrile prior to GC analysis and often an oxygen-specific detector (O-FID) was necessary. However, simple GC methods in combination with a flame ionization detector (FID) have been developed using capillary columns of different polarities, both common columns for the analysis of gasoline [HARDMAN ET AL., 1993; LOCKWOOD AND CADDOCK, 1983] and columns with more polar stationary phases [PAULS, 1995; PRICE AND SAUNDERS, 1984]. Recently, a GC method using a special capillary column designed for the separation of MTBE (J & W DB-MTBE) in combination with a photoionization detector (PID) [CUMMINS ET AL., 2001].
In this study a simple GC method by use of GC equipped with a FID and a SE-54 capillary column for the improved separation of MTBE from hydrocarbons in gasoline was developed.

3.1.3 Experimental

3.1.3.1 Materials and Methods

MTBE and ethyl *tert*-butyl ether (ETBE) standards were obtained in the highest commercially available purity (>97 %, Fluka). Standard solutions of ETBE in distilled methanol (>99.9%, Fluka) were prepared to a concentration of 1 mg/mL, cooled at 4 °C and used within 4 weeks. Gasoline samples were collected in 10 mL vials at different gas stations of big companies in the Frankfurt area during filling a vehicle. The vials were completely filled and sealed. The samples were cooled, transported to the laboratory and were analysed within 24 hours. For the analysis, 1 µL gasoline was diluted by 500 µL methanol and 60 µL of the ETBE standard solution (1 mg/mL) was added. The method was developed by use of GC/ MS and applied to GC.

3.1.3.2 Instrumental

The GC (Thermo Quest Finnigan Trace GC 2000) coupled to the MS (Thermo Quest Finnigan Voyager GC/ MS) and the GC (Fisons Instruments GC 8160) used for the application were adapted to the same conditions: The injector port was kept at 240 °C and the split mode with a ratio of 1:20 was used. Liners with an inner diameter of 0.75 mm and a 50 m SE-54 capillary column (Chromatographie Service GmbH, Langerwehe, Germany) with a film thickness of 5 µm were installed. The GC column temperature was first held at 30 °C for 23 min, then increased to 240°C at a rate of 20 °C/min and held for 40 min. Helium and

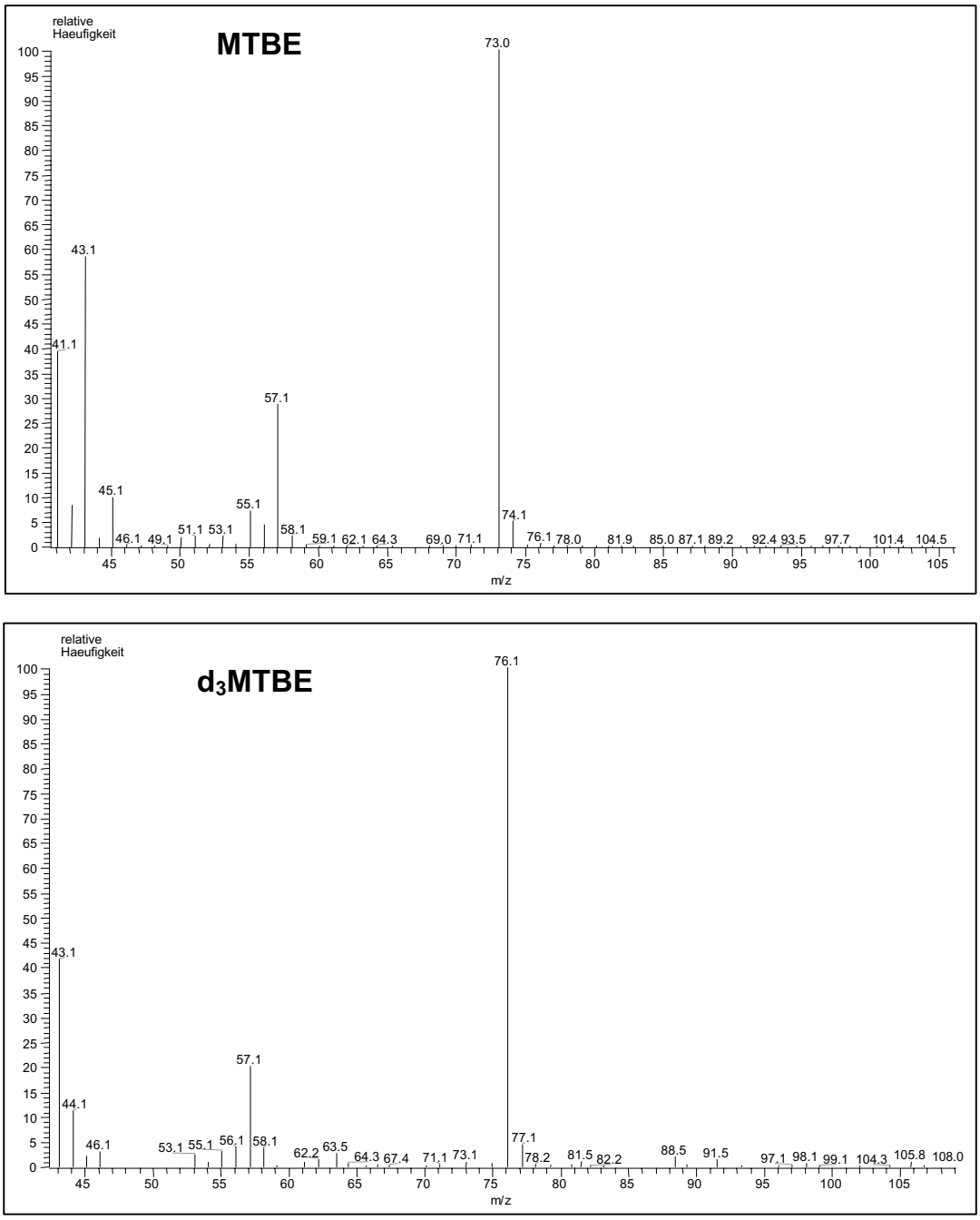


Figure 3-1 Mass spectra of methyl tert-butyl ether (MTBE) and deuterated methyl tert-butyl ether (d_3MTBE) which served as internal standard (70 eV).

Hydrogen served as carrier gas at a flow of 0.8 mL/min for the GC-MS and the GC, respectively. The detector temperature of the GC was 300 °C.

Peak detection and integration was carried out by use of Xcalibur (Version 1.0, GC/ MS) and Chromcard for Windows (1.19-7?, GC). The scan range of the GC-MS included 40 - 600 *m/z*.

The mass spectrometer was tuned to optimize signals from 40 - 125 *m/z*. MTBE standards were used in order to determine the characteristic ions and the retention times used for identification of MTBE in the gasoline samples. Mass chromatography of *m/z* 73, *m/z* 57 and *m/z* 43 in full scan mode was used for qualifying MTBE. Mass spectra of MTBE and d_3MTBE are shown in Figure 3-1. The MTBE signals could be checked with respect to superimposition by other compounds, especially by 2-methyl pentane, since the analyses were carried out in the full scan mode. ETBE served as internal standard for quantitation of gasoline samples analysed by the GC.

3.1.4 Results and Discussion

The GC method was developed by choosing an appropriate capillary column, liner and internal standard for the analysis from the literature. The carrier gas flow, split ratio and oven temperature program were adjusted in order to provide an optimal separation of MTBE from other analytes. It is known that particularly 2-methyl pentane, which is a common compound in gasoline tends to superimposition with MTBE. By use of a GC equipped with an O-FID detector system the alkanes are not detected and a clean MTBE peak can be quantified. However, in the present case a GC method for the analysis of MTBE in combination with the very common and versatile FID detector is described. Complex back-flushing and column switching systems are not required.

Amongst the common capillary columns used for the analysis of gasoline [HARDMAN ET AL., 1993; LOCKWOOD AND CADDOCK, 1983] a SE-54 (94% methyl silicone gum, 5% phenyl and 1% vinyl) was preferred to a 100% dimethyl silicone gum stationary phase because MTBE tends to superimposition with 2,3-dimethyl butane by use of the latter. The retention window between 2- and 3-methyl pentane was chosen for the elution of MTBE due to the absence of superimposition with other hydrocarbons from gasoline. The method was established using GC/ MS in the full scan mode. The identification and quality of the separation of MTBE was controlled by use of its primary, secondary and tertiary ions *m/z* 73, 57 and 43, respectively.

The separation of MTBE from 2-methylpentane is not reached completely but to an acceptable extent. Reasonably good separation was also reached by HARDMAN ET AL. [1993] using helium as carrier gas and a low starting temperature of the GC oven (25 °C). In the present study improvement of the analytical conditions was achieved by the use of hydrogen instead of helium and an increase of the oven starting temperature to 30 °C. Additionally the column length could be shortened from 60 m [HARDMAN ET AL., 1993] to 50 m. For the

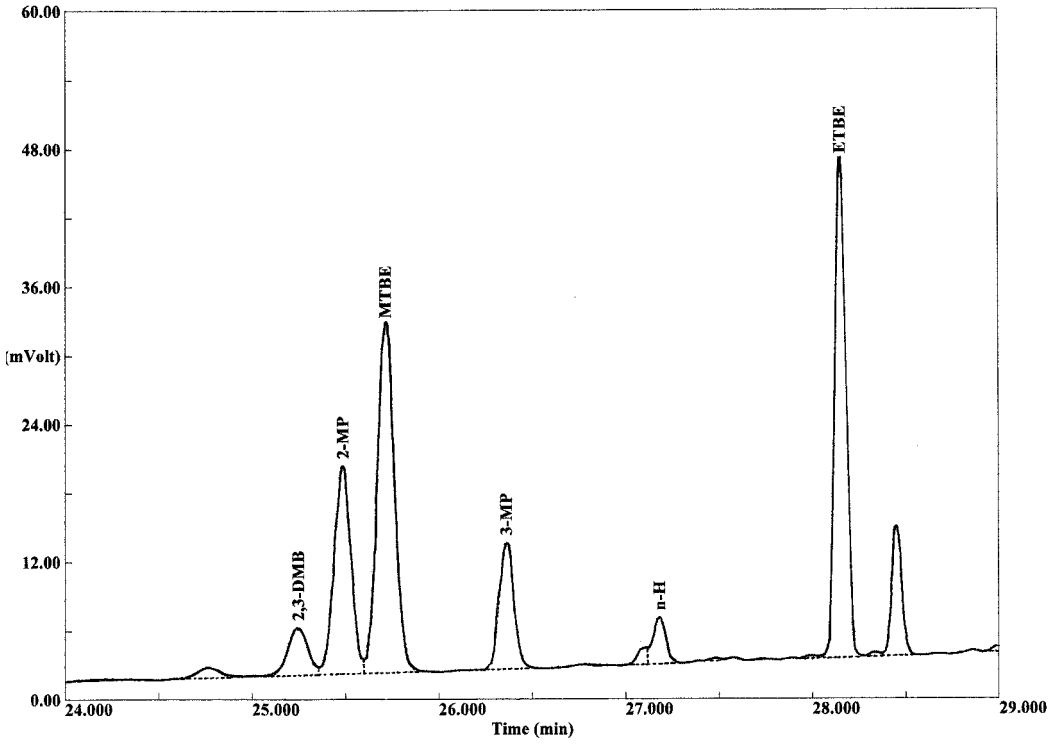


Figure 3-2 Typical partial gas chromatogram of super premium unleaded gasoline. Ethyl tert-butyl ether (ETBE) served as internal standard.

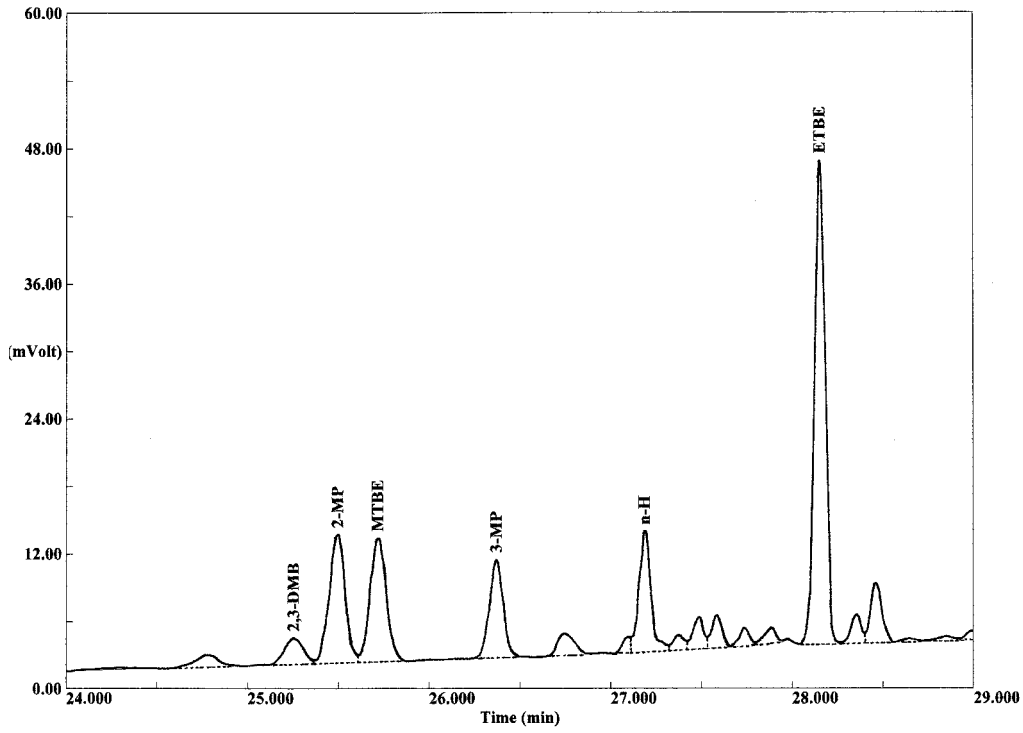


Figure 3-3 Typical partial gas chromatogram of Euro super unleaded gasoline. Ethyl tert-butyl ether (ETBE) served as internal standard.

quantitation of MTBE, fluorobenzene [ROSE ET AL., 1998; RAESE ET AL., 1995], methyl propyl ketone or methyl ethyl ketone [DGMK, 1994], di-isopropylether (Dr. Thölmann, Infracor, Marl, Germany, personal communication), *tert*-butanol, butyl ethyl ether [DISANZO, 1990] and methyl [2H3] *tert*-butyl ether [ACHTEN AND PÜTTMANN, 2000] have been used as internal standards. For the present study ETBE was used because of its physico-chemical similarity with MTBE, its reasonably good stability and its clear separation from other analytes in the GC of all types of gasoline. Due to the possible use of ETBE as an octane enhancer in gasoline every sample was injected without internal standard prior to quantitative analysis to reasure that ETBE was not present in the sample. ETBE was not detected in any sample. However, it has to be considered that ETBE is used as gasoline additive in the U.S., France and Italy [KATZEN ET AL., 1997].

Optimization of the temperature program showed best results when the iso temperature of 30 °C was held as long as possible for the separation of MTBE from 2-methylpentane and when the temperature was increased to a high rate before the elution of MTBE in order to receive a narrow peak shape. The analysis time was set to 30 min and an analytical cycle

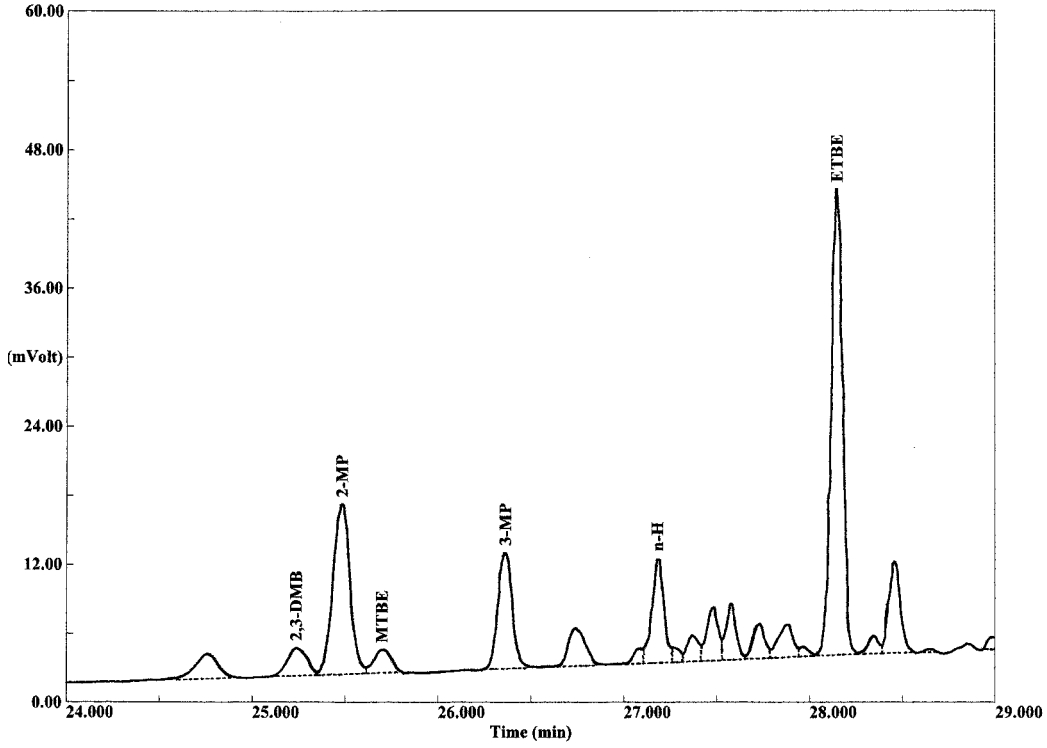


Figure 3-4 Typical partial gas chromatogram of regular unleaded gasoline. Ethyl tert-butyl ether (ETBE) served as internal standard.

including the cleaning of the chromatographic column was complete in 94 min. Due to the generally slow carrier gas flow velocity of 0.8 mL/min an analysis of MTBE was time-consuming. In order to reduce the analysis time the carrier gas flow was accelerated to 1.5 mL/min once the conditioning temperature of 240 °C was reached and faster reconditioning was received. Before the next sample analysis the gas flow was reset again to 0.8 mL/min.

After the optimizing procedure by GC/ MS, the developed method was applied to the GC-analysis of regular unleaded, Euro super unleaded, super premium unleaded and „Optimax“ gasoline (Figures 3-2 - 3-4 and Table 3-1).The results of 39 analysed gasoline samples of different oil companies show average MTBE contents of 0.4 % (w/w) for regular unleaded, 9.8 % (w/w) for super premium unleaded and 11.9 % (w/w) for the new „Optimax“ gasoline. The amounts of MTBE for Euro super unleaded gasoline generally vary from 0.3 to 1.3 % (w/w) although the amount in Euro super from company 2 with an average of 3.5 % (w/w) is remarkably higher. The MTBE conversion ratio volume % to weight % in petrol is very close to 1 (at 15 °C) in typical European commercial petrol grades [MEF, 2001].

The obtained data are comparable to other published data and show an increase in the use of MTBE in Germany in gasoline since 1992/ 1993. Average MTBE values of 0.2, 1.7 and 8.7 % (w/w) in regular, Euro super and super premium unleaded gasoline were measured in 1992/ 1993 [DGMK, 1994] and 0.3, 1.6 and 6.0 % (w/w) in 1996, respectively [CONCAWE, 1998]. In 1998 super premium was blended by a few big companies with a median of 8.2 % MTBE (w/w), whereas the value for all measured companies was 7.7 % (w/w) [BREUM, 1998]. It can be concluded that particularly the bigger companies offer „cleaner-burning“ gasoline and add higher amounts of MTBE to the fuel. The use of the oxygenate in super premium has increased to 9.8 % (w/w) in 1999. A slight increase to 0.4 % (w/w) can also be observed regarding regular unleaded gasoline whereas the source data for Euro super fluctuate significantly. Therefore, the data basis is not sufficient for the development of an average value.

3.1.5 Conclusion

The developed GC method in combination with a FID is a simple and reliable means for the determination of MTBE in gasoline. Optimal analysis was achieved by use of a 50 m SE-54 capillary column with a film thickness of 5 µm, a liner with an inner diameter of 0.75 mm and a low gas flow of 0.8 mL/min. The oven temperature program that was set to 30 °C for

Table 3-1 Analysed samples of regular, Eurosuper, super premium unleaded gasoline and "Optimax" gasoline. The samples were taken at Frankfurt am Main in 1999 and 2000.

Company	Location of sampling	Date of sampling	Regular unleaded [% w/w]	Euro super unleaded [% w/w]	Super premium unleaded [% w/w]	Optimax [% w/w]
1	Stresemannallee	08/03/99	0.3	1.3	12.2	-
	Autobahn 66	08/26/99	0.4	0.9	6.8	-
	Sossenheim	08/26/99	-	-	11.0	-
2	Kennedyallee	08/03/99	0.5	4.2	10.8	-
	Kennedyallee	08/24/99	-	2.9	-	-
	Friedberger Landstraße	07/19/99	-	3.4	9.0	-
	Autobahn 66	08/26/99	0.6	3.5	10.2	-
3	Kennedyallee	08/03/99	0.5	0.3	10.1	-
	Kennedyallee	08/24/99	-	0.6	-	-
	Kelkheim	08/26/99	0.5	-	10.7	-
4	Friedberger Landstraße	07/19/99	0.3	0.4	9.5	-
	Kennedyallee	08/03/99	0.3	0.7	8.5	-
	Kennedyallee	08/24/99	-	0.4	-	-
	Hansaallee	07/19/99	-	-	9.1	-
	Friedberger Landstraße	06/27/00	-	-	-	13.6
	Friedberger Landstraße	06/29/00	-	-	-	10.4
	Kennedyallee	06/29/00	-	-	-	11.6
Average			0.4	-	9.8	11.9

23 min, then increased to 240 °C at a rate of 20 °C/min and held for 40 min. The separation of the gasoline component 2-methylpentane from MTBE is reached sufficiently for reliable quantiation. The method is also useful for the measurement of other ethers, for example ETBE when another internal standard is chosen.

3.2 Determination of MTBE in Surface Water by Use of Direct Solid-Phase Microextraction (SPME)/ Gas Chromatography - Mass Spectrometry (GC/ MS)

3.2.1 Abstract

A new method based on solid-phase microextraction (SPME) has been developed for the determination of methyl *tert*-butyl ether (MTBE) in surface water at sub-ppb concentrations. The combination of SPME and GC/ MS can be applied for the detection of MTBE at low concentrations if limiting factors are optimized. Best results were obtained with a cooled (5 °C) 75 µm poly(dimethylsiloxane)/ Carboxen (PDMS/ Carboxen) fiber at a sample temperature of 18 - 19 °C and a sodium chloride concentration of 10 %. 60 min extraction time showed the best compromise between time-consuming and effective extraction in a 1.5 mL vial filled with the water sample. The detection limit under the conditions of a defined signal to noise ratio of 10:1 is 10 ng/L and the relative standard deviation for replicate injections was 8 % (n = 10).

3.2.2 Introduction

The detection of the gasoline oxygenate methyl *tert*-butyl ether (MTBE) in the aquatic and atmospheric environment has led to concern about its environmental fate due to the large amounts that are now being produced in the United States. In Germany the use of MTBE as a fuel additive also significantly increased since 1985. MTBE concentrations emitted from non-point sources were detected in the United States in urban air [ZOGORSKI ET AL., 1998; POORE ET AL., 1997; GROSJEAN ET AL., 1998], stormwater [DELZER ET AL., 1996; LOPES AND BENDER, 1998], streams [ZOGORSKI ET AL., 1998; REISER AND O'BRIEN, 1998], lakes that are significantly loaded with recreational watercraft [BOUGHTON AND LICO, 1997; REUTER ET AL., 1998; BAEHR AND ZAPECZA, 1998] and shallow urban groundwater [SQUILLACE ET AL., 1995, 1996, 1997A,B AND 1999; DALY AND LINDSEY, 1996; STACKELBERG ET AL., 1997; LANDMEYER ET AL., 1996].

Common analytical methods using purge-and-trap or direct aqueous injection (DAI) were reported not to detect less than 60 ng/L (reporting level 200 ng/L), 83 ng/L and 50 ng/L of MTBE respectively [RAESE ET AL., 1995; ROSE ET AL., 1998; CHURCH ET AL. 1997]. These methods could not be applied for the analysis of MTBE in surface waters in Germany due to its currently low concentration. A DAI method by ZWANK ET AL. [2002] is in preparation. A

detailed summary of the methods used for MTBE analysis in water is given by SCHMIDT ET AL. [2001]. The present study describes the development of a method for analysis of MTBE in water samples at a lower detection limit. The method is based on solid-phase microextraction (SPME) [NILSSON ET AL., 1998; THOMAS ET AL., 1996; CZERWINSKI ET AL., 1996; HEGLUND AND TILOTTA, 1996] in combination with gas chromatography coupled to mass spectrometry (GC/ MS).

3.2.3 Experimental Section

3.2.3.1 Materials and Methods

Standards were made from 10,000 µg/L stock solutions containing MTBE or isotopically labeled MTBE ($MTBd_3E$). Each compound was obtained in the highest commercially available purity (>97 %, Fluka). The standard solutions were cooled at 4 °C and used within 4 weeks. SPME was performed with a SPME manual sampling holder equipped with a 75 µm poly(dimethylsiloxane)/ Carboxen (PDMS/ Carboxen) fiber, a 65 µm poly(dimethyl-siloxane)/ divinylbenzene (PDMS/ DVB) fiber or a 65 µm Carbowax/ divinylbenzene (CW/ DVB) fiber from Supelco (Figure 3-5). The sample temperature during extraction in the liquid varied from 5 - 30 °C and ice was used for cooling (5 °C) of the manual holder. Sodium chloride (>99.5 %, Merck), sodium hydroxide (99 %, Merck) and hydrochloric acid (30 %, Merck) served to optimize the SPME conditions. The stirring of the sample during extraction evoked by a magnetic stirring-bar (3 mm, Supelco) was performed at a velocity of 895 - 900 rev/min. The volumes of the sample vials varied from 1.5, 4, 10 to 250 mL. The immersion depth of the fibers in the water phase during extraction was 1 cm. The extraction time varied from 5 - 300 min. The pH was measured by a Universal Meter Multiline P4 (Wissenschaftlich-Technische Werkstätten). Water samples were collected using standard water sampling techniques for volatile organic compounds (VOCs) [KOTERBA ET AL., 1995], except that the samples were not preserved by acidification.

3.2.3.2 GC/ MS

Thermal desorption of the extracted compounds was effected by inserting the SPME fiber into the GC injector port (3.8 cm) kept at 240 °C. The fiber remainded in the injector after desorption for subsequent reconditioning of 30 min. Throughout the study, no MTBE residues

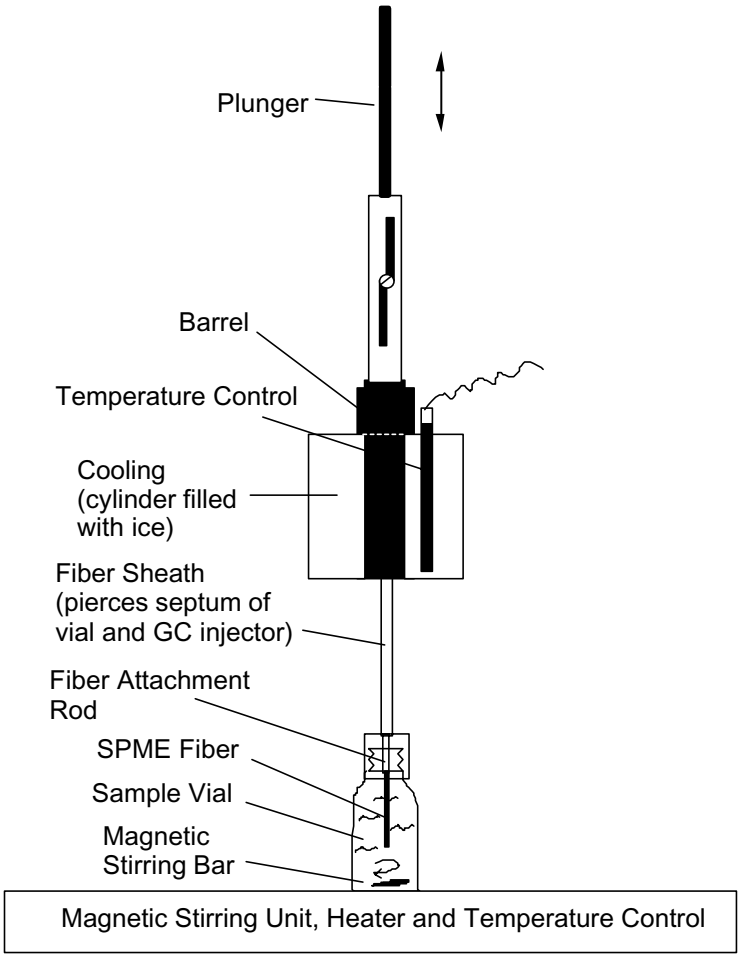


Figure 3-5 Schematic model of solid-phase microextraction (SPME) with cooling of the manual sampling holder.

were found left on the SPME fiber after each reconditioning. The split mode with a ratio of 1:20 and a 0.75 mm (inner diameter) liner were used. The GC column temperature was first held at 35 °C for 1 min, then increased to 100 °C at a rate of 10 °C/min before further increased to 240 °C at a rate of 50 °C/min and held for 40 min. Separation of the analytes was performed by gas chromatography (Fisons Instruments GC 8060) using a 50 m SE-54 capillary column (CS) with a film thickness of 5 μm. Helium served as carrier gas at a pressure of 70 kPa.

Peak detection and identification were carried out using a mass spectrometer (Fisons Instruments MD 800), and integration of peak areas were carried out using Masslab software (Windows, Version 1.3). The scan range included 50 - 600 *m/z*. The mass spectrometer was

tuned to optimize signals from 50 - 125 *m/z*. Mass chromatography of *m/z* 73 in full scan mode was used for the quantitation of MTBE. The detection limit was defined by a 10:1 signal to noise ratio.

Previously, MTBE has been quantified by the ion *m/z* 73 and qualified by the secondary and tertiary ions *m/z* 57 and 43 and fluorobenzene has been used as internal standard [ROSE ET AL., 1998] For the present study, $MTBd_3E$ at a concentration of 10 µg/L was used as internal standard because of its close physico-chemical similarity with MTBE. GC/ MS-analysis of pure $MTBd_3E$ revealed *m/z* 76 as the appropriate qualifying and quantitation ion and *m/z* 57 as the secondary ion. The fragment *m/z* 73 was detected as a trace only and could be neglected. On the other hand MTBE did not show any ions *m/z* 76. This allows the use of the ion *m/z* 76 of $MTBd_3E$ for qualifying and quantifying MTBE. The tertiary ion m/z 43 could not be measured because the scan range was 50 - 600 *m/z*. The MTBE signals could be checked with respect to superimposition by other compounds since the analyses were carried out in the full scan mode. In each case the 73 *m/z* ion was only composed of MTBE. In a sample containing both MTBE and $MTBd_3E$, the retention times differed by 0.035 min only.

3.2.4 Results and Discussion

The analysis of MTBE in water is usually carried out by purge-and-trap according to U.S. EPA method 524.2 or comparable methods with a detection limit of 60 ng/L and a reporting level of 200 ng/L [RAESE ET AL., 1995]. Recently, a long-term method detection level (LT-MDL) of 83 ng/L for small amounts of MTBE using purge-and-trap has been reported [ROSE ET AL., 1998]. Another approach of improving analytical sensitivity is the use of direct aqueous injection. For MTBE, detection limits of 50 ng/L by use of single-ion detection (selected ion monitoring, 73 *m/z*), of 100 ng/L using multiple ion-detection (selected ion monitoring, 73, 57, 43 *m/z*) and of 10 µg/L analysed by full scan of all atomic masses (full scan mode, 41 - 150 *m/z*) could be achieved [CHURCH ET AL., 1997]. However, the amounts of MTBE in surface water in Germany to date are significantly lower than in the United States due to less consumption of the oxygenate as a fuel additive. In order to monitor the current amounts of MTBE in rain and surface waters in Germany, a new method with lower detection levels had to be developed and is described here. The method applied here is based on solid-phase microextraction (SPME) combined with gas chromatography/ mass spectrometry (GC/ MS).

In the first step of method development, distilled water spiked with a concentration of 10 µg/L MTBE was used. As starting conditions, SPME of 4 mL water in a 4 mL vial for 30 min at 18 - 19 °C sample temperature were chosen. First, the affinity for MTBE of three different solid-phases was tested by the use of a 65 µm fiber of CW/ DVB, a 65 µm PDMS/ DVB fiber both for polar analytes with low and high molecular mass respectively and a 75 µm PDMS/ Carboxen fiber for trace-level volatiles. The 75 µm PDMS/ Carboxen fiber revealed the best recovery rate of 5.6 %, the PDMS/ DVB fiber absorbed 2.6 % MTBE, whereas the CW/ DVB fiber could only extract 0.2 % of MTBE from the water sample. This is in agreement with the expected results because sensitivity increases as the volume of coating increases [ZHANG ET AL., 1996]. The PDMS/ Carboxen fiber was used for further optimizing experiments only.
In a second step, the influence of temperature on the extraction yield was investigated. It is known that sample temperature and fiber temperature have an important impact on the amount of analyte extracted according to the following equation [ZHANG ET AL., 1996]:

$$n = \frac{K_{fs}\, V_f\, C_0\, V_s}{K_{fs}\, V_f + V_s}$$

K_{fs} is the fiber/ sample partition coefficient, V_f and V_s are the volumes of the fiber and the sample respectively and C_0 is the starting concentration of the analyte. N is the amount of analyte absorbed on the fiber. Generally, an increase in the temperature difference between fiber and water sample leads to an increase in K_{fs} values and thus in an increase in sensitivity [ZHANG ET AL., 1996]. Under starting conditions, the extraction yields of MTBE were measured at 5, 11, 14, 18-19, 22, 25 and 30 °C sample temperature with and without additional cooling of the fiber to 5 °C. The results have shown highest extraction yields at 18 - 19 °C sample temperature and simultaneous cooling of the fiber to 5 °C (Figure 3-6). About 20 times more MTBE could be extracted at the optimal temperature in comparison to extraction at 5 °C sample temperature. A constant increase of the extraction yield with increasing temperature up to the maximum could be observed, followed by a rapid decrease at higher values. At the temperature range of the highest extraction yield, cooling of the fiber to 5 °C resulted in an increase of MTBE recovery by about 24 %.
Another factor influencing the fiber/ sample partition coefficient is the ionic strength of the sample. The addition of salt to the aqueous samples can either reduce or increase the recovery of analytes. Consequently, the effect of adding salt to a sample should be evaluated for the

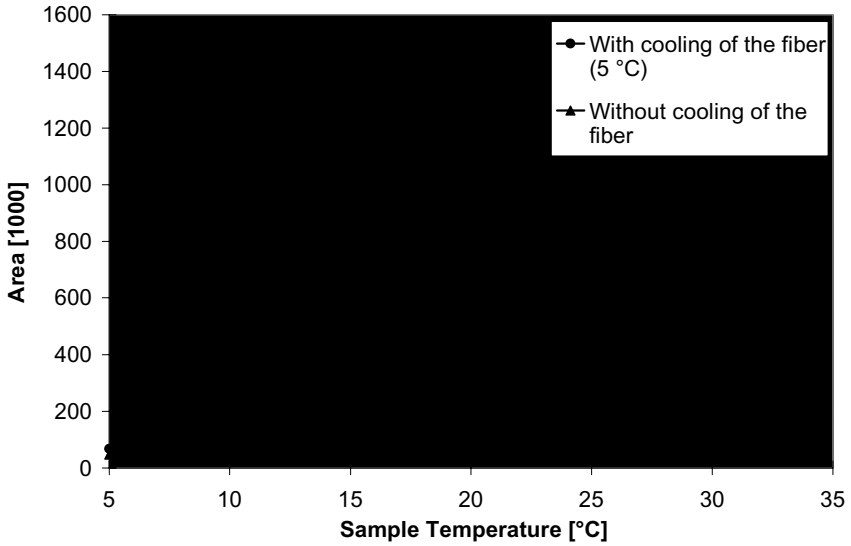


Figure 3-6 Influence of sample temperture on extraction yield with and without cooling of the fiber (distilled water sample with a concentration of 10 µg/L methyl tert-butyl ether (MTBE)).

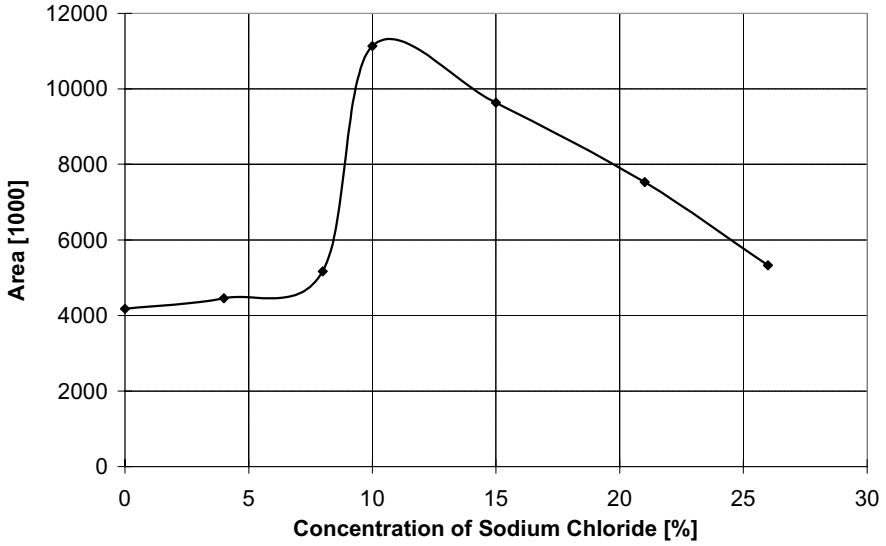


Figure 3-7 Influence of sodium chloride on extraction yield (distilled water sample with a concentration of 10 µg/L methyl tert-butyl ether (MTBE)).

analytes of interest [ZHANG ET AL., 1996; SUPELCO, 1996]. To study the effect of salt on the MTBE recovery rate, water samples containing different concentrations of sodium chloride have been analysed (Figure 3-7). Results have shown that at concentrations of 4 % and 8 %

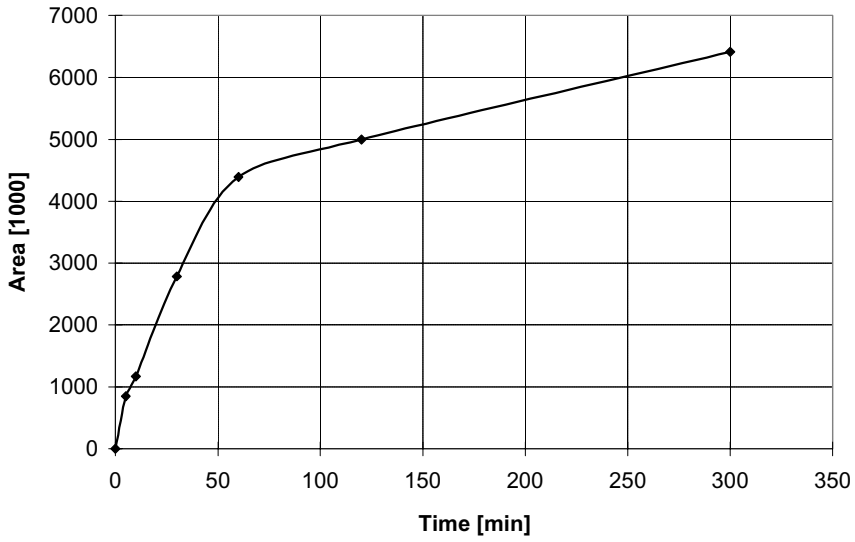


Figure 3-8 Influence of extraction time on extraction yield (distilled water sample with a concentration of 10 µg/L methyl tert-butyl ether (MTBE)).

sodium chloride, extraction yields of MTBE increased slightly in comparison to a sample without salt. The highest extraction yield of 166 % in relation to the sample without salt was reached at a sodium chloride concentration of 10 %. Upon further addition of sodium chloride to a content of 15 %, 21 % and finally up to 26 %, the extraction yield decreased again constantly.

The influence of time on the extraction yield of an analyte by use of SPME has been investigated before [GROTE AND LEVSEN, 1998]. 30 min were recommended as the best compromise between time-consuming and effective extraction. The results of the extraction yield of MTBE depending on the extraction time are shown in Figure 3-8. The amount of MTBE recovered at a total extraction time of 300 min has been defined as 100 %. After 5, 10, 30 and 60 min the extraction yields were 13, 18, 43 and 68 %, respectively. At a further extension of the extraction time the extraction yields increased only slowly. Doubling of the extraction time from 30 min to 60 min results in an 25 % increase of the extraction yield. Therefore, for further studies an extraction time of 60 min was selected.

The pH value of the aqueous sample had an insignificant impact on the extraction yield. The highest yield was received at pH 7. At lower and higher pH values (pH 2, 4 and 9), the deviation from the maximum extraction yield did not exceed 11 %.

Vials of four different volumes (1, 5, 4, 10 and 250 mL) were used for extraction of the water All vials were filled with distilled water spiked with MTBE at a concentration of 10 µg/L up to 3 mm below the septum of the vial in order to avoid contact with the manual holder. The

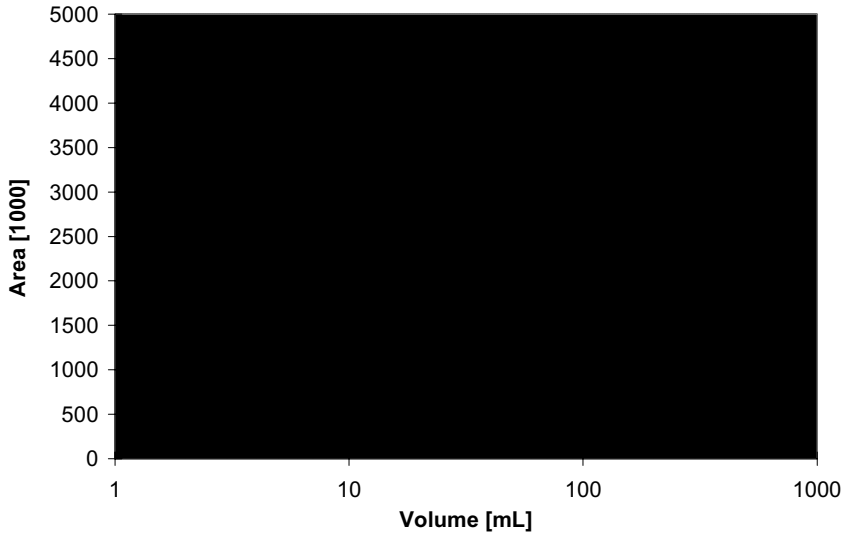


Figure 3-9 Influence of sample volume on extraction yield (distilled water sample with a concentration of 10 µg/L methyl tert-butyl ether (MTBE)).

highest amounts of MTBE were recovered at the lowest sample volume of 1.5 mL. A decreasing recovery of MTBE was observed with increasing sample volumes (Figure 3-9). A further reduction of the sample volume is limited by the size of the stirring-bar.
After optimizing the analytical conditions using the PDMS/ Carboxen fiber only, the recovery rates of the three different fibers were measured again by use of these conditions. Results have shown that the PDMS/ Carboxen fiber still provides the highest recovery rate (8.0 %) in comparison to the PDMS/ DVB (4.1 %) and CW/ DVB fiber (0.3 %). Optimal results were achieved by extraction of 1.5 mL water sample volume in a 1.5 mL vial for 60 min at 18 - 19 °C sample temperature and cooling of the fiber to 5 °C. Sodium chloride was added at a concentration of 10 % and the pH was not adjusted to a specific value. Integration of peaks for MTBE using distilled water spiked with MTBE at a concentration of 10 µg/L gave a relative standard deviation for replicate injections of 8 % (n = 10). The detection limit under the conditions of a defined signal to noise ratio of 10:1 was 10 ng/L by use of distilled water spiked with MTBE or river water.

3.3 Improvement of the Method: SPME in Headspace

3.3.1 Abstract

A simple and rapid method for the determination of methyl *tert*-butyl ether (MTBE) in water by headspace-solid-phase microextration (headspace-SPME) at sub-ng/L concentrations is described [ACHTEN ET AL., 2001B]. Using a cooled SPME fiber coated with 75 µm poly(dimethylsiloxane)/ Carboxen and heating the sample to 35 °C about 4 times more MTBE is extracted compared to SPME extraction with the fiber placed into the water sample. Stable analytical conditions with a detection limit of 10 ng/L are achieved. By use of a sample volume of 4 mL in a 10 mL vial, a sodium chloride content of 10% (w/w) and an extraction time of 30 min the total time of an analytical cycle was optimized to 39 min. Precise linearity of R^2 >0.9991 and R^2 >0.9916 in the calibration range from 20 - 5000 ng/L and 20 - 100 ng/L both in addition to blanks, respectively, and relative standard deviations of 10% (100 ng/L, long-term) and 11% (20 ng/L, short-term) are presented. The recovery is well within accepted limits of 83 - 118% at a concentration of 100 ng/L and even close to it at trace-levels of 20 ng/L (96 - 125%). The presented data at a concentration of 100 ng/L are tested by statistical methods and show results for the *T* test at the 95 % confidence level. Due to the large concentration range the method is well suited for the monitoring of MTBE in the aquatic environment.

3.3.2 Introduction

With increasing numbers, MTBE concentrations are detected in the atmospheric and aquatic environment on the American continent and in Europe [ZOGORSKI ET AL., 1998; GAFFNEY ET AL., 1999; KLINGER ET AL., 2000; ACHTEN AND PÜTTMANN, 2000; ACHTEN ET AL., 2001A, 2002A AND B]. The introduction of MTBE into the subsurface by point sources (eg. leaking underground storage tanks) can represent a risk for groundwater not only due to the low odor and taste threshold of 20 µg/L but also because the toxicity of the ether is not yet clearly understood. The closure of drinking water wells due to contamination with MTBE has been described [HAPPEL ET AL., 1998]. In Germany, super premium unleaded gasoline, regular unleaded gasoline and the new „Optimax“ gasoline showed average MTBE contents of 9.8,

0.4 and 11.9 % (w/w) in 1999, respectively. The values for Euro super unleaded gasoline varied from 0.4 to 4.2 % (w/w) [ACHTEN AND PÜTTMANN, 2001A].

Common analytical methods using flame or photoionization detection in combination with a single capillary column are not suitable for the analysis of MTBE due to possible false-positive signals that are the result of superimposition with other hydrocarbons [HALDEN ET AL., 2001]. Only by use of mass spectrometry that produces mass-to-charge ratios (*m/z*) of compound-specific fragments it is possible to identify MTBE. Methods using purge-and-trap or direct aqueous injection are in general not suitable for the analysis of low MTBE concentrations in surface water, precipitation and drinking water because these methods were reported not to detect less than 50 ng/L [RAESE ET AL., 1995; ROSE ET AL., 1998; CHURCH ET AL., 1997; BRAUCH ET AL., 2000A].

Solid-phase microextraction (SPME) has been successfully used to rapidly concentrate volatile organic compounds [CASSADA ET AL., 2000; BOCCINI ET AL., 1999; JAMES AND STACK, 1997; NILSSON ET AL., 1998; SUPELCO, 1995; DERMIETZEL AND STRENGE, 1999; GAINES ET AL., 1998] and a wide variety of other organic compounds in aqueous and other matrices [PAWLISZYN, 1997; SCHIMMING ET AL., 1999; MÖDER ET AL., 1997; WERRES ET AL., 2000; ABDEL-REHIM ET AL., 2000; YU ET AL., 1999; NG ET AL., 1999; LLOYD ET AL., 1998; JÄRVENPÄÄ ET AL., 1999]. However, the detection limits reported for volatile organic compounds have only recently been lower than 50 ng/L [CASSADA ET AL., 2000; SCHIMMING ET AL., 1999]. MTBE was analyzed by SPME-GC/ MS directly in the water sample and a detection limit of 8 ng/L was received. Generally, the method focuses on higher concentrations of MTBE because it is calibrated by 40, 2000 and 4000 ng/L and the recovery rate is calculated by use of a concentration of 800 ng/L. Additionally, blank analysis is not described [CASSADA ET AL., 2000]. Recently, a sensitive method for the analysis of human blood using headspace-SPME-GC/ MS providing limits of quantitation of 5 and 25 ng/L for benzene and toluene, respectively, a calibration range from 5 - 5000 ng/L and a detailed investigation of blanks has been reported [SCHIMMING ET AL., 1999]. The successful performance of SPME directly in the aqueous samples or in the headspace depends on the specific target analyte and its physico-chemical properties. Several volatile organic compounds were measured by use of SPME directly in the water sample compared to extraction in the headspace and best recoveries were found at both the two locations of extraction depending on the target analyte [SUPELCO, 1995]. MTBE was not included in this study. SPME measurements of MTBE by extraction from the water phase have been reported to lead to a detection limit of 10 ng/L [ACHTEN AND PÜTTMANN, 2000]. The disadvantage of

this method is the rapid pollution of the ion source due to the introduction of abundant low volatile organic matter and of water.
The present study describes the development of a stable and sensitive method for analysis of MTBE in water samples by headspace-SPME/ GC-MS and represents an improvement of the existing method [ACHTEN AND PÜTTMANN, 2000]. Detailed data concerning calibration, linearity, blanks, accuracy and precision are presented. Due to the independence of the matrix from the aqueous samples, the method can also be applied to wastewater.

3.3.3 Experimental Section

3.3.3.1 Materials and Methods

Calibration Standards of MTBE at concentations of 20, 100 and 5000 ng/L and isotopically labeled MTBE (d_3MTBE) at a concentration of 10 µg/L were prepared from 2000 µg/mL stock solutions (Fluka) and from pure d_3MTBE (>99%, Fluka), respectively. Each compound was obtained in the highest commercially available purity. The first dilution steps were performed by use of methanol whereas further preparation of the standard solutions was carried out using distilled, subsequently boiled and for the preparation of the standard solutions cooled water (1 °C). In order to minimize volatilization of the ethers during preparation of the standards it was necessary to push the plunger of the syringes very slowly at several intervals of about 5 mm into the water in order to allow the chemicals to dissolve. When the plunger was pushed continuously without stops unacceptable calibration curves were received. The standard solutions were cooled at 4 °C and used within 4 weeks. For the optimization process of this method MTBE solutions at a concentration of 100 ng/L were used. Additionally, standards at a concentration of 20 ng/L were used for the investigation of precision and accuracy. 40 µL of the d_3MTBE standard solution which served as internal standard was added to the spiked water samples for MTBE quantitation.
Water samples were collected in 100 mL sample vials (brown glass) using standard water sampling techniques for volatile organic compounds [KOTERBA ET AL., 1995]. The analyzed samples were collected in the years 1999 to 2001. Precipitation was collected by use of a rainwater collector (Eigenbrodt) with a lid that opened for precipitation only. It was placed on the top of a building in order to eliminate other inputs. All samples were analyzed within 4 weeks after collection.

3.3.3.2 HS-SPME/ GC-MS

SPME was performed by a SPME manual sampling holder equipped with a 75 µm poly(dimethylsiloxane)/ Carboxen (PDMS/ Carboxen) fiber from Supelco. The manual sampling holder was cooled to 0°C by use of a cryostat (Haake, Berlin) during extraction. Sodium chloride (>99.5 %, Merck) was used in the highest purity commercially available. The stirring of the sample during extraction by a magnetic stirring-bar (3 mm, Supelco) was performed at a velocity of 895 - 900 rev/min. The sample temperature was controlled by heating the magnetic stirring unit. Vials of 10 mL were used in combination with septa (Dichtring Sil/ PTFE blau-transparent 3,0 mm, Loch 11 mm, Chromatographie Zubehör Trott, Kriftel) that were made of two different thicknesses in order to seal at the outer ring and be easily pierced by the SPME sampling holder in the inner part.
The immersion depth of the fiber into the headspace above the aqueous sample during extraction was 0.8 cm. Due to the location of the fiber into the headspace and thereby no direct contact to the matrix of the water samples the fiber was significantly more often reusable (about 1000 times) than by locating the fiber into the liquid.
Thermal desorption of the extracted compounds from the SPME fiber was effected by inserting it into the GC injector port (3.8 cm) kept at 260 °C. The fiber remainded in the injector for 10 min. Note that due to numerous injections of the SPME sampling holder the septum of the injector port needed to be sealed by use of a closed needle, when the sampling holder was absent. The split mode with a ratio of 1:20 and a 0.75 mm (inner diameter) liner were used. The GC column temperature was first held at 50 °C for 1 min, then increased to 200 °C at a rate of 10 °C/min and held for 20 min at final temperature. Separation of the analytes was performed by gas chromatography (Thermo Quest CE Instruments Trace GC 2000 Series) using a 50 m SE-54 capillary column (CS) with a film thickness of 5 µm. Helium served as carrier gas at a pressure of 70 kPa.
Peak identification and quantitation were carried out using a mass spectrometer (Thermo Quest Finnigan Voyager GC/ MS) using the software Xcalibur (Version 1.0). Scanning of the fragments was performed in full scan mode with a scan range of 40 - 600 *m/z*. The mass spectrometer was tuned to optimize signals from 40 - 125 *m/z*. Mass chromatography of *m/z* 73 and *m/z* 76 in full scan mode was used for the quantitation of MTBE by the internal standard d_3MTBE, respectively. This was possible because the mass spectrum of MTBE shows no fragments *m/z* 76 and the spectrum of d_3MTBE only consists of neglectable traces of the fragment *m/z* 73. The detection limit was defined by a 10:1 signal to noise ratio.

3.3.3.3 Starting Conditions

The starting conditions for the optimization process were extraction directly in the aqueous sample, 11.2 mL water sample in a 11.2 mL vial, 60 min extraction time, 10 % sodium chloride content, 18 to 19 °C sample temperature, 75 min for a total analytical cycle (analysis and cooling), 15 min reconditioning time of the fiber in the injector port and a GC oven temperature program that started at 35 °C for 1 min, then increased to 100 °C at a rate of 10 °C/min before further increased to 240 °C at a rate of 50 °C/min and held for 40 min [ACHTEN AND PÜTTMANN, 2000].

3.3.4 Results and Discussion

3.3.4.1 Method development

3.3.4.1.1 Location of the Fiber and Sample Volume

By use of the reported SPME/ GC-MS method [ACHTEN AND PÜTTMANN, 2000] where MTBE is extracted directly from the aqueous sample by immersing the fiber into the water the detection system of the MS showed fluctuations of sensitivity due to the pollution of the ion source by low volatile organic compounds and water. In order to overcome these problems extraction in the headspace above the aqueous sample was investigated. By locating the fiber into the headspace stable conditions of the MS and about 4 times more MTBE and d_3MTBE could be extracted compared to direct immersion into the water.

The optimal quotient of aqueous volume to headspace volume for headspace analysis in 10 mL vials was measured by varying the sample volume at amounts of 0.5, 1, 2, 3, 4 and 5 mL. The results are shown in Figure 3-10. The extracted amounts of MTBE and d_3MTBE increased continuously with increasing sample volume, reached a maximum yield at an aqueous volume of 4 mL which is equal to 67% headspace and again decreased at a sample volume of 5 mL. At a volume of 4 mL about 50% more of both ethers were extracted in comparison to extraction of 3 and 5 mL sample volumes. For further investigation headspace analysis above a 4 mL water sample volume was used.

3.3.4.1.2 Extraction Time and Time of the Total Analytical Cycle

Most of the total time for an analytical cycle is used for the extraction time in combination with the GC oven temperature program and the reconditioning time of the fiber. When MTBE is analyzed by direct SPME extration in the water sample, 60 min are necessary in order to achieve a detection limit of 10 ng/L [ACHTEN AND PÜTTMANN, 2000]. Locating the fiber into the headspace provided faster equilibrium between the two phases. Extraction times of 15, 25, 30, 35, 45 and 60 min were investigated and the results are shown in Figure 3-11. The extraction yield was constantly low (about 57 %) until 25 min, followed by a rapid increase at 30 min of about 30 % and a slower at 35 min of about 13%. Further extension of the extraction time did not increase the amount of MTBE and d_3MTBE significantly but at 45 and 60 min the fluctuations of the peak areas increased leading to higher standard deviations.

An extraction time of 30 min represents a good compromise between a good extraction yield and an acceptable exposure time.

For the oven conditions a starting temperature of 50 °C for 1 min was used. Then the temperature was increased to 200 °C at a rate of 10 °C and held for 20 min. The separation of the ethers from other compounds did not change significantly, nor did the peak shape but the GC oven needed less time for cooling to 50 °C in comparison to 35 °C used previously [ACHTEN AND PÜTTMANN, 2000]. The reduced maximum temperature from 240 to 200 °C and conditioning time of the GC oven from 40 to 20 min provided the same cleaning effect of the whole system. Moreover, the desorption and reconditioning time of the fiber was reduced from 15 to 10 min. After a desorption time of 10 min no memory effects were observed even with samples with high analyte concentrations. The described improvements led to a reduced time of the total analytical cycle (extraction, analysis and cooling) from 75 [ACHTEN AND PÜTTMANN, 2000] to 39 min.

3.3.4.1.3 Sample Temperature

The temperature of the sample influences the volatilization of the ethers into the headspace. By use of direct SPME extraction from water best results were obtained at a sample temperature of 18 to 19 °C [ACHTEN AND PÜTTMANN, 2000]. At this temperature low extraction yields were received by use of headspace-SPME. Measurements at 15, 20, 25 and 30 °C showed increasing amounts of extracted ethers to a maximum at 35 °C where 47 % more was extracted in comparison to 15 °C (Figure 3-12). At 40 °C the average value was significantly lower and the standard deviation increased.

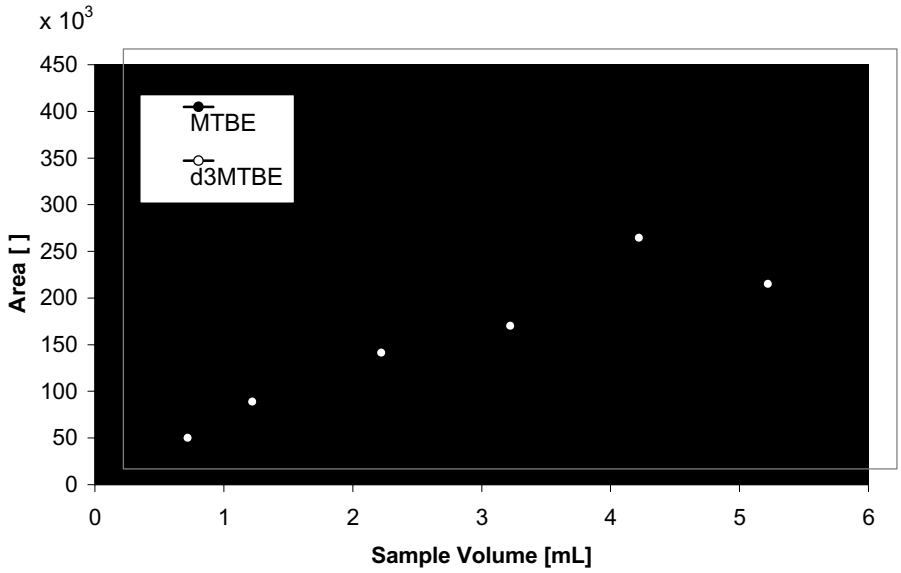


Figure 3-10 Influence of sample volume on extraction yield (distilled water sample with a concentration of each 100 ng/L methyl tert-butyl ether (MTBE) and $d_3$methyl tert-butyl ether (d_3MTBE), 3 replicates).

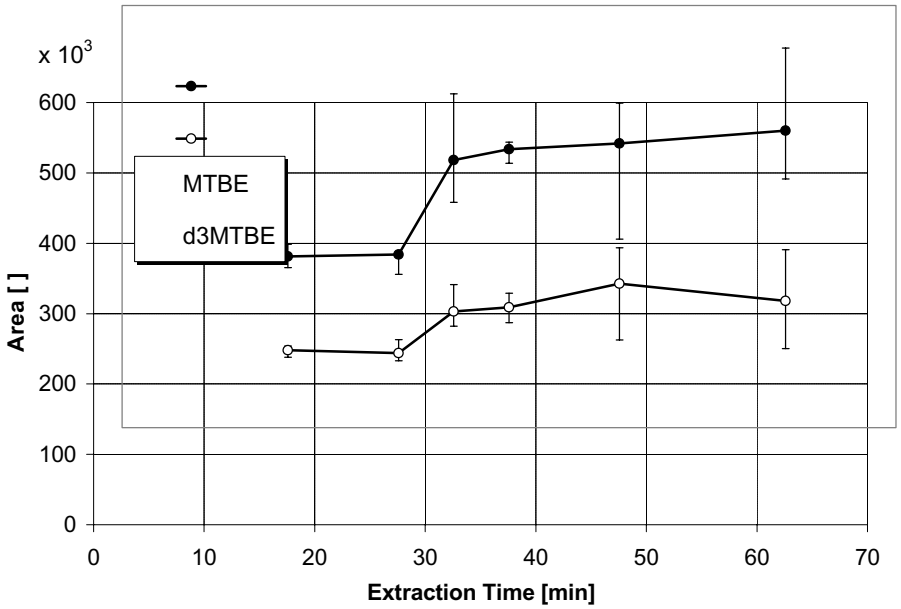


Figure 3-11 Influence of extraction time on extraction yield (distilled water sample with a concentration of each 100 ng/L methyl tert-butyl ether (MTBE) and $d_3$methyl tert-butyl ether(d_3MTBE), 3 replicates).

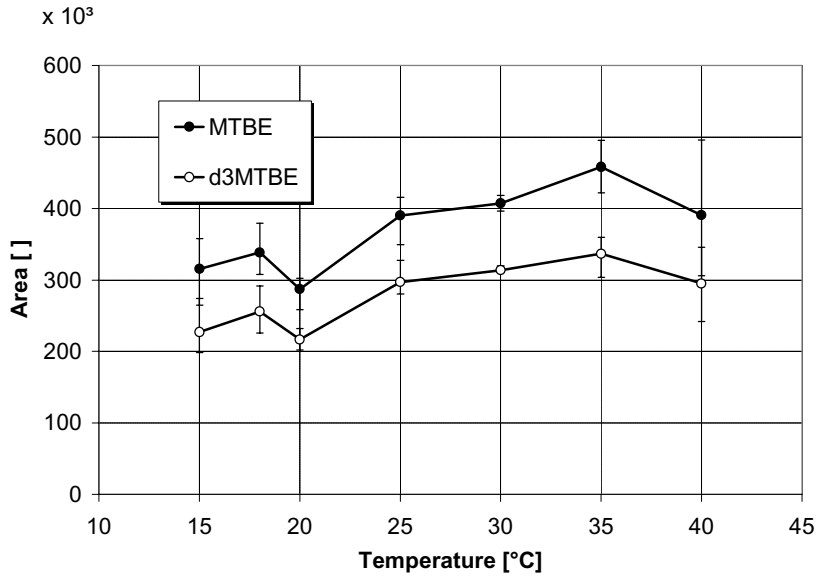


Figure 3-12 Influence of sample temperature on extraction yield (distilled water sample with a concentration of each 100 ng/L methyl tert-butyl ether (MTBE) and $d_3$methyl tert-butyl ether (d_3MTBE), 3 replicates).

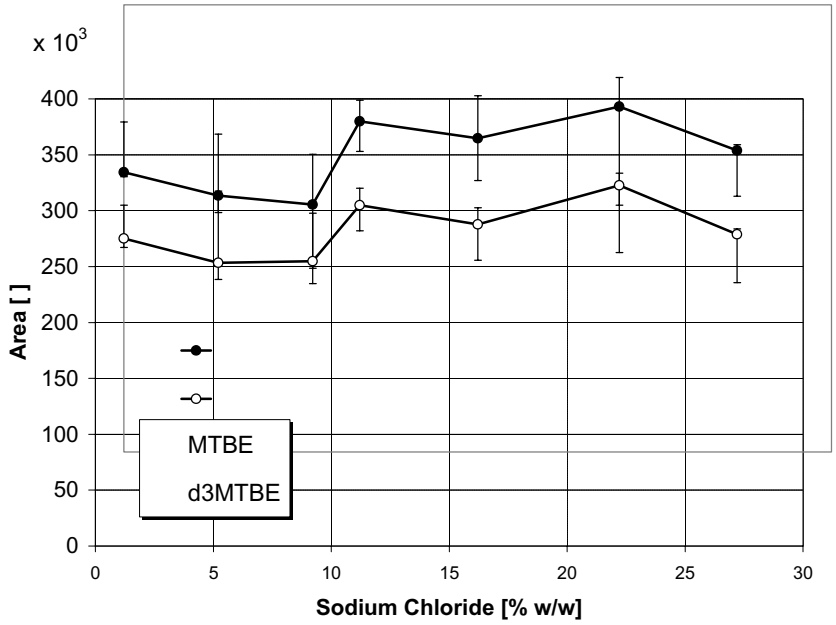


Figure 3-13 Influence of sodium chloride on extraction yield (distilled water sample with a concentration of each 100 ng/L methyl tert-butyl ether (MTBE) and $d_3$methyl tert-butyl ether (d_3MTBE), 3 replicates).

3.3.4.1.4 Sodium Chloride Concentration

To study the effect of salt on the MTBE recovery rate, water samples containing different concentrations of sodium chloride have been analyzed (Figure 3-13). Results have shown that at concentrations of 0,4 and 8 % (w/w) sodium chloride, extraction yields of MTBE are about 25 % (w/w) lower than at 10 % (w/w) sodium chloride. Upon further addition of sodium chloride to a content of 15 and 21 % (w/w) the extraction yields fluctuated to a large extent before decreasing at addition of 26 % (w/w) salt. 10 % (w/w) were chosen to provide best results. At the same concentration best results were obtained at direct SPME extraction from water although the kinetic mechanisms are totally different [ACHTEN AND PÜTTMANN, 2000].

3.3.4.2 Method Validation

3.3.4.2.1 Blanks

As described by SCHIMMING ET AL. [1999] for benzene and toluene at trace-level concentrations, MTBE can also not be eliminated completely from the analytical system. Step-by-step investigations of the source of contamination revealed the GC-MS system as the contamination source. Even several hours of heating the injection system, the oven and the ion source did not remove traces of MTBE completely (Figure 3-14). This was possible only after the installation of a new capillary column and liner and similarly cleaning of the ion source (Figure 3-15). The remaining blanks correspond to a MTBE concentration of about 45 ng/L at the four-point-calibration (blank, 20, 100, 5000 ng/L) and of about 15 ng/L at the three-point-calibration at a lower level (blank, 20, 100 ng/L). Fortunately, these blank values are very constant (relative standard deviation (RSD = 9 %) as long as samples of extremely high concentrations (in the µg/L - mg/L range, eg. groundwater near leaking underground storage tanks) are excluded or diluted. SCHIMMING ET AL. [1999] reported blank concentrations for benzene and toluene of 30 and 15 ng/L, respectively with a RSD $\leq$6 %.

3.3.4.2.2 Calibration and Linearity

Calibration samples of different concentration ranges from 20 to 5000 ng/L (including blanks) were measured in order to investigate linearity (Table 3-2). Very precise linearity of R^2 = 0.9991 to1.0000 over 3 orders of a magnitude were received at the four-point-calibrations (blank, 20, 100 and 5000 ng/L). For measurements in the range of 20 to 100 ng/L (including blanks) three-point-calibrations (blank, 20 and 100 ng/L) were used in order to

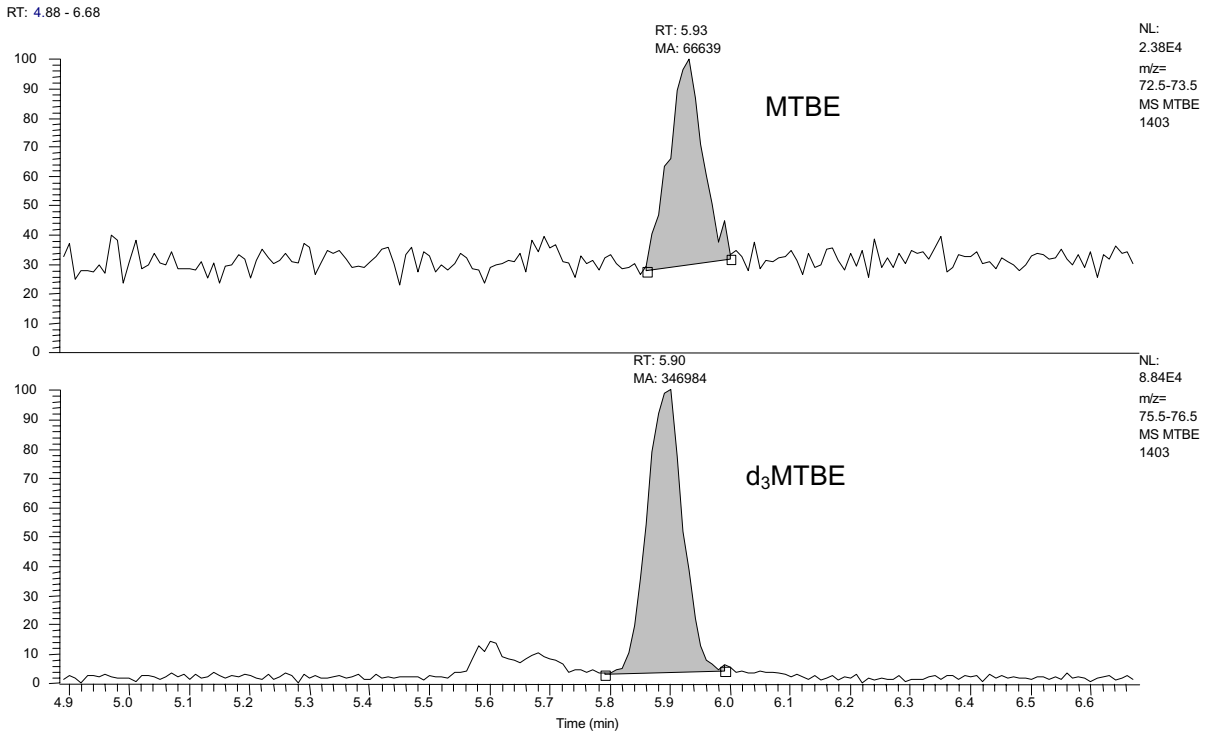


Figure 3-14 Mass chromatogram of m/z 73 (methyl tert-butyl ether (MTBE), blank, top) and m/z 76 ($d_3$methyl tert-butyl ether (d_3MTBE), 100 ng/L, bottom) between sample analysis.

reduce MTBE contamination by injection of higher concentrated standards into the GC-MS system. The calibration curves showed good linearity with coefficients of $R^2 = 0.9916$ to 1.0000.

CASSADA ET AL. [2000] reported linearity in the range of 40 - 4000 ng/L with coefficients of R^2 higher than 0.98 by use of direct SPME extraction of MTBE from water. By use of the same type of SPME fiber (Carboxen/ PDMS) as used in this study a correlation coefficient of $R^2 = 0.999$ at low concentrations for benzene and toluene extracted by headspace-SPME was published for a calibration range of 25 - 5000 ng/L [SCHIMMING ET AL., 1999]. A second calibration curve ranging from 5 - 250 ng/L was set for trace-level concentrations, but no correlation coefficient was published.

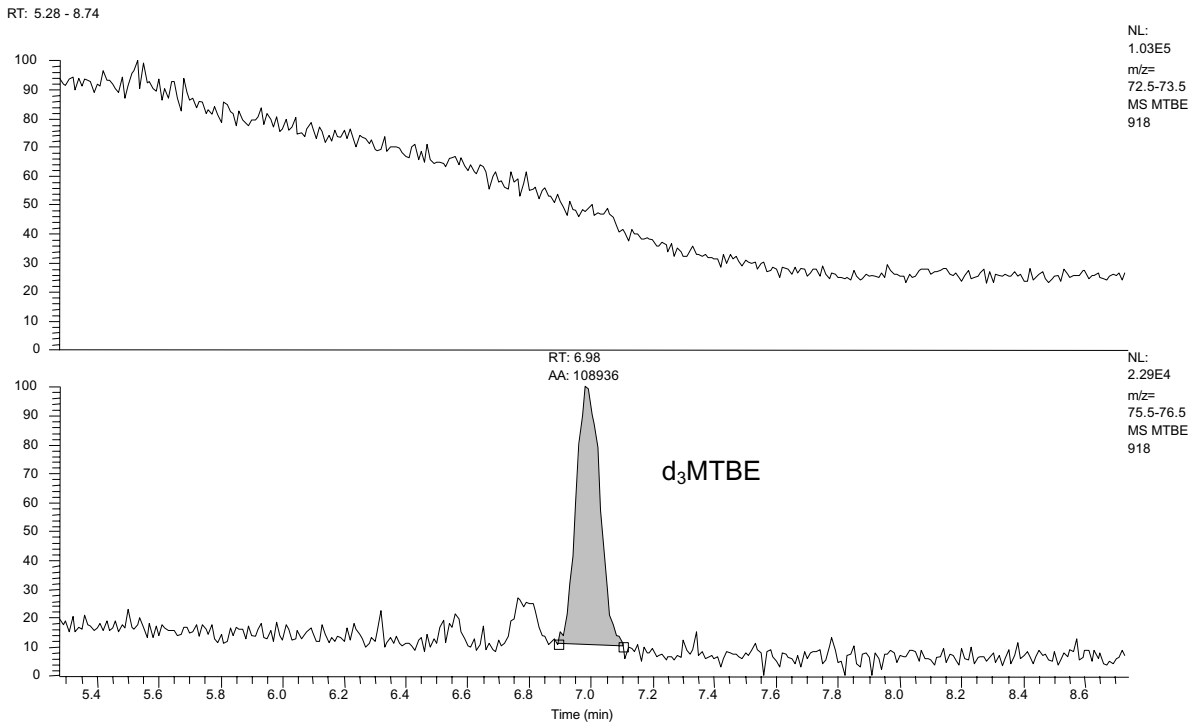


Figure 3-15 Mass chromatogram of m/z 73 (methyl tert-butyl ether (MTBE), blank, top) and m/z 76 ($d_3$methyl tert-butyl ether (d_3MTBE), 100 ng/L, bottom) after the installation of a new capillary column, new liner and similarly cleaning of the ion source.

3.3.4.2.3 Accuracy and Precision

Short-term (one day) and long-term (7 months) performance of this analytical method was investigated by the analysis of MTBE in 53 reagent-water spikes at a concentration of 100 ng/L. The recovery was 83 - 118 % with a mean of 99 % and a RSD of 10 % (Figure 3-16). This result is well within quality-control criteria for comparable U.S. EPA methods that recovery should be within accepted limit of 80 to 120 % with a RSD less than 20 % [U.S. EPA, 1992]. Analysis of 10 low-level standard solutions at 20 ng/L MTBE in January 2001 show recoveries of 96 - 125 % with a mean of 113 % and a RSD of 11 %. Method performance is close to the quality-control criteria even at these very low concentrations. By direct MTBE extraction from the water sample using a concentration of 42 ng/L and measurement in the single ion monitoring mode (SIM) recoveries of 98 to 107% were observed [CASSADA ET AL., 2000]. SCHIMMING ET AL. [1999] also measured in the SIM mode but performed extraction in the headspace and reported a RSD of 7.6 % and 14.5 % for benzene and toluene, respectively by use of a concentration level of about 220 ng/L. The

Table 3-2 Calibration ranges, equations and correlation coefficients of four-point-calibrations (blank, 20, 100 and 5000 ng/L) and three-point-calibrations (blank, 20 and 100 ng/L) for concentrations of methyl tert-butyl ether (MTBE) in the range of about 80 to 5000 ng/L and about 10 to 80 ng/L, respectively.

Calibration range [ng/L]	Calibration equation	Correlation coefficient R^2
blank-20-100-5000	y = 0.0117x + 0.4926	0.9999
	y = 0.0090x + 0.3584	1.0000
	y = 0.0118x + 0.4421	0.9999
	y = 0.0118x + 0.3899	0.9999
	y = 0.0086x + 0.3507	1.0000
	y = 0.0091x + 0.4185	0.9998
	y = 0.0087x + 0.4314	0.9998
	y = 0.0085x + 0.4872	0.9998
	y = 0.0078x + 0.5205	0.9991
	y = 0.0082x + 0.5107	0.9995
	y = 0.0092x + 0.4368	0.9999
	y = 0.0128x + 0.3681	1.0000
	y = 0.0089x + 0.5950	0.9999
	y = 0.0098x + 0.5404	0.9999
	y = 0.0078x + 0.2051	1.0000
	y = 0.0084x + 0.2216	1.0000
	y = 0.0098x + 0.3756	1.0000
Average	y = 0.0097 + 0.4479	1.0000
blank-20-100	y = 0.0227x + 0.1856	0.9943
	y = 0.0084x + 0.2216	1.0000
	y = 0.0098x + 0.1826	0.9916
	y = 0.0189x + 0.0836	0.9974
Average	y = 0.0150 + 0.1684	0.9958

presented data at a concentration of 100 ng/L were tested by statistical methods [MILLER AND MILLER, 1993] and showed results for the *T* test at the 95 % confidence level. The results indicate that this method is capable of providing sensitive and accurate MTBE analysis in water. Recently, this method has been internationally validated for its quality of low-level measurement of MTBE in water (<500 ng/L) by comparison to 27 other laboratories using different methods. From 28 participants, only 6 laboratories - including this method - provided results within the proposed RSD of 80 – 120 % [KOLB, 2001; SCHUHMACHER AND FÜHRER, 2001].

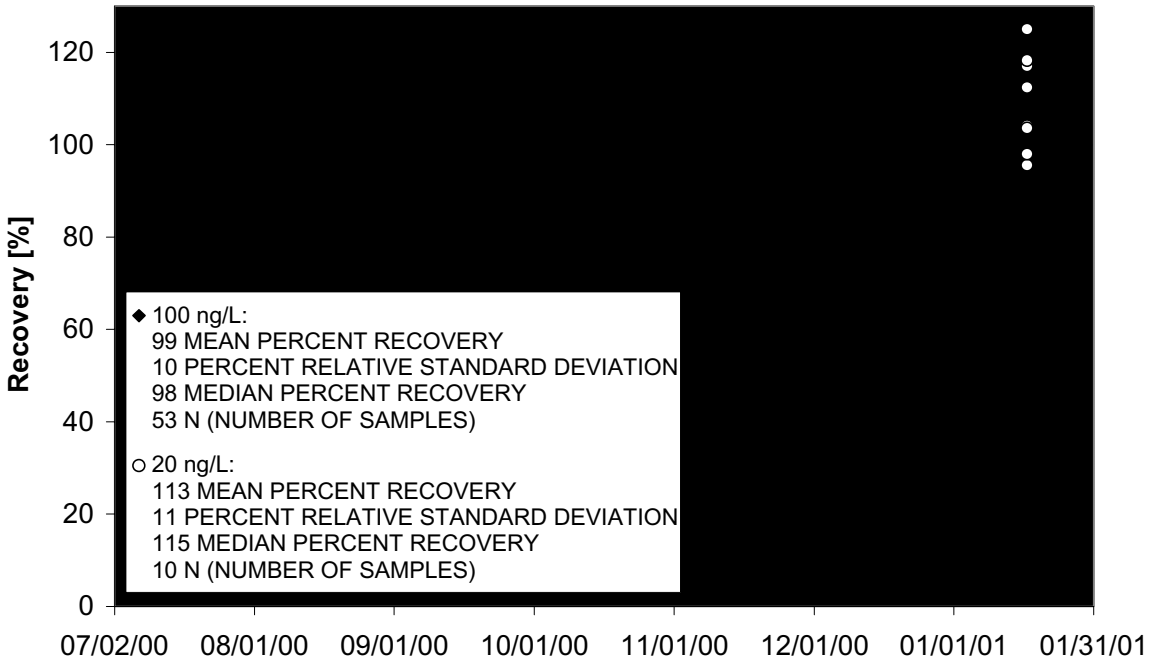


Figure 3-16 Percent recovery of methyl tert-butyl ether (MTBE) from distilled water spikes at 100 ng/L (long-term measurement) and 20 ng/L (short-term measurement).

It is noteworthy that several volatile organic compounds other than MTBE are also detected by the method. The measurement of characteristic gasoline constituents like benzene, toluene, ethylbenzene and xylenes (BTEX) by use of the described method is currently being investigated [KOLB, 2001].

3.3.4.2.4 Field Study

In the years 1999 to 2001 different aqueous samples including river water, precipitation, urban runoff, wastewater, industrial wastewater, drinking water and groundwater were analyzed. The field data demonstrate that even lowest concentrations of MTBE in precipitation and drinking water (10 - 50 ng/L) can be determined by the SPME method reported here. The linear range of the method is sufficiently large to also monitor higher concentrations in river water, urban runoff and wastewater. Groundwater samples and industrial wastewater at higher concentrations of MTBE and possibly additional aromatic compounds like BTEX have to be diluted before analysis (1:100). By use of liquid or headspace SPME extraction for analysis of MTBE matrix effects occur if high concentrations

(mg/L) of BTEX and trimentylbenzenes are present and significantly lower sensitivity of the method was reported [BLACK AND FINE, 2001].

3.3.5 Conclusions

A method for the determination of MTBE in water is reported which is based on solid-phase microextraction [ACHTEN ET AL., 2001B]. By sampling in the headspace of the water about 4 times more MTBE was extracted compared to locating the fiber directly into the water sample. Additionally, rapid pollution of the ion source by water and less volatile organic matter in the water could be avoided. The fiber could be reused about 1000 times which is significantly more than compared to use of the fiber in the water. Using a poly(dimethylsiloxane)/ Carboxen fiber for extraction fixed to a cooled manual sampling holder in combination with a heated sample, limits of quantitation with a detection limit of 10 ng/L are achieved which allow the determination of MTBE in precipitation, drinking water, river water, urban runoff, wastewater, industrial wastewater and groundwater. Reliable and simple MTBE measurements at trace-levels in water samples become increasingly important as the use of the oxygenate has led to detectable amounts in the aquatic environment and even in the drinking water system. The method reported here is well suited for the monitoring of MTBE.

4 MTBE CONCENTRATIONS IN ENVIRONMENTAL WATER SAMPLES IN GERMANY

4.1 MTBE in Urban and Rural Precipitation

4.1.1 Abstract

The use of the oxygenate methyl *tert*-butyl ether (MTBE) in gasoline has led to detectable concentrations in urban and rural air up to 160 ppb_V. Results from MTBE measurements in precipitation have not been reported so far. In the present study, 120 samples of precipitation collected at 17 sampling locations all over Germany have been analyzed for their MTBE content. In precipitation samples, MTBE was detected in wintertimes only with a maximum concentration of 85 ng/L. Measurement at Frankfurt/M city from 9/6/00 - 3/12/01 provided for 49 % of the data concentrations in the range of 30 - 85 ng/L (n = 17). Sampling in winter 2000/ 2001 at several german cities and rural locations showed that MTBE is more often detectable in urban (86 %, n = 78) than in rural (18 %, n = 42) precipitation. By comparing the results with corresponding temperatures and amounts of precipitation, it can be concluded that the detection of MTBE in urban precipitation is observed at ambient temperatures lower than about 10 - 15 °C. Moreover, the first precipitation after a dry period accumulates more MTBE than precipitation during or at the end of a wet period (wash-out effect). Highest concentrations occured in snow samples. Corresponding mean air equilibrium concentrations of 0.04 ppb_V (urban samples) and 0.01 ppb_V (rural samples) are calculated. This is about one order of a magnitude lower than year round and summertime measurements in the U.S. and in Switzerland. Urban runoff (n = 12) and corresponding precipitation sampling indicates that urban runoff might be composed of about 20 % MTBE that is already transported by air and precipitation whereas about 80 % may be attributed to direct uptake of vehicle emissions and leakage near the road during precipitation.

4.1.2 Introduction

MTBE has been detected in the atmospheric and aquatic environment on the American continent and in Europe with increasing numbers [ZOGORSKI ET AL., 1998; GAFFNEY ET AL., 1999; KLINGER ET AL., 2000; JOHNSON ET AL., 2000; BRAUCH ET AL., 2000A; ACHTEN AND PÜTTMANN, 2000 AND 2001B; ACHTEN ET AL., 2001A, 2002A AND B]. The introduction of MTBE into the subsurface by point sources (e.g. leaking underground storage tanks) can

represent a risk for groundwater not only due to the low odor and taste threshold of 20 µg/L but also because the toxicity of the ether is not yet clearly understood. The closure of drinking water wells due to contamination with MTBE has been described [HAPPEL ET AL., 1998]. Only a few results of analyzed atmospheric MTBE concentrations have been reported so far. Measurement of MTBE concentrations in the air of mega cities showed amounts of 0.2 – 17 ppb_V (mean = 6.6 ppb_V, n = 44), 40 - 160 ppb_V (n = 16) and 1.28 ppb_V (n = 1) in Porto Alegre/ Brazil [GROSJEAN ET AL., 1998], Mexico City/ Mexico [GAFFNEY ET AL., 1999] and Kairo/ Egypt [DOSKEY ET AL., 1999], respectively. In Brazil gasoline is described to be oxygenated by 15 % (w/w) MTBE, in Mexico [BRAVO AND TORRES, 2000] and Egypt only by 5 and 3 – 10 % (w/w), respectively [DOSKEY ET AL., 1999]. Emissions released from motor vehicle traffic [FRASER ET AL., 1998; POULOPOULOS AND PHILIPPOPOULOS 2000, KIRCHSTETTER ET AL., 1996] and volatilization at gasoline stations during refueling [GAFFNEY ET AL., 1999; VAINIOTALO ET AL., 1998 AND 1999, VAYGHANI AND WEISEL, 1999] are thought to be the main sources. Near gasoline stations, peak MTBE concentrations of up to 14,000 ppb_V based on short-term measurements were detected in the atmosphere. However, mean values at pump islands are in the range of tens to hundreds ppb_V (Table 4-1). Only recently, average atmospheric MTBE concentrations were investigated for a combination of urban and rural sampling sites and thereby represent the MTBE situation in larger areas rather than only at urban sites. Mean measured atmospheric MTBE concentrations of 0.25 ppb_V (median) [BAEHR ET AL., 1999], 0.82 ppb_V [BENDER ET AL., 2000] and 0.66 ppb_V [BUWAL, 1999] sampled in New Jersey/ U.S., California/ U.S. and Switzerland were calculated to correspond to aqueous concentrations of 90 (median), 350 and 373 ng/L, respectively. The Henry's Law coefficient calculation published by BAEHR ET AL. [1999] was also used for calculations in this study (Figure 2-4). It has been shown that atmospheric MTBE might be responsible for low concentrations in surface and groundwater [PANKOW ET AL., 1997; BAEHR ET AL., 1999 AND 2001; BENDER ET AL., 2000]. In the Glassboro Comprehensive Urban Study/ New Jersey, MTBE is measured in precipitation [ZOGORSKI ET AL., 1998] but to our knowledge data have not yet been published. In the present study, MTBE concentrations in precipitation in Germany are presented. To our knowledge this is the first publication of MTBE measurements in precipitation apart from the analysis of MTBE in stormwater [DELZER ET AL., 1996; LOPES AND BENDER, 1998].

Table 4-1 Atmospheric methyl tert-butyl ether (MTBE) concentrations (ppb_V) at gasoline stations.

Number of samples	Minimum	Mean	Maximum	Sampling location	MTBE concentration in gasoline in the investigated area	Reference
	[ppb_V]	[ppb_V]	[ppb_V]		[% w/w]	
32	0.14	2.6	33	four main compass points on the service station perimeter	11	VAINIOTALO ET AL:, 1998
16	67	207	368	pump island		
167	< 5.5	901	13 934	breathing zone during refueling	5	VAINIOTALO ET AL:, 1999
8		63		pump island		
46	< 6.3	300	1300	in vehicle cabin during refueling	15	VAYGHANI AND WEISEL, 1999
36	< 5	29	170	pump island		

4.1.3 Sampling

An amount of 42 precipitation samples were collected at Frankfurt/M city from 1998 to 2001 by use of a rainwater collector (Eigenbrodt) with a lid that opened for precipitation only. It was placed on the top of a building (without emissions from fuel burning) in order to eliminate other input. All samples collected in this study represent spot samples. Rainwater or melted snow was analyzed for MTBE from December 1998 to the end of August 2000 monthly. Spot samples in winter 1999/ 2000 were collected once per month at the moment when the ambient temperature decreased significantly and/ or the first precipitation fell after a longer dry period. Since September 2000, samples were collected after every precipitation event.

78 rural rain water samples at Schmücke, Neuglobsow, Waldhof, Brotjacklriegel, Zingst, Deuselbach, Schauinsland and Westerland in winter 2000/ 2001 were collected at the monitoring stations by the Umweltbundesamt. Samples from the Taunus-Observatorium (Feldberg) were collected by the Meteorologisches Institut of the University Frankfurt/ M. The Laboratory of the Berliner Umweltsenator provided precipitation samples from Berlin.

Further urban water samples from Köln, Stuttgart, Hamburg and Berlin and rural precipitation at Altenholz-Klausdorf and Rade were collected in the winter 2000/ 2001 by use of a rain water collector that was placed on the top of a building or on the ground far away from any traffic. From 09/06/00 - 12/19/00 a few (n = 12) urban runoff samples were collected by dipping the sample bottles into ditches on the border of a high traffic road which is situated 500 m from the precipitation sampling at Frankfurt/M. Urban runoff and corresponding precipitation samples were taken at the same day. All samples were stored in 100 mL sample bottles (brown glass) that were acidified before by concentrated hydrochloric acid (33 %). The bottles were completely filled with no headspace left and cooled to 4 °C. Analysis was performed within 3 weeks after collection. The bottles were heated to 110 °C for 5 hours before use.

4.1.4 Results and Discussion

4.1.4.1 Precipitation

The long-term precipitation measurement at Frankfurt/M city from 1998 to 2001 showed detectable MTBE concentrations in wintertimes only (Figure 4-1). In winter 1998/ 1999 and 1999/ 2000 with longer sampling intervals only a few samples indicated MTBE concentrations up to 70 ng/L in rain or snow. Detailed sampling in winter 2000/ 2001 wth shorter intervals confirmed the former data, with MTBE values up to 85 ng/L. Strong fluctuations of the MTBE concentrations are probably the result of the high sampling frequency because samples were taken daily if enough precipitation for the analysis could be collected (e.g. even after heavy rain that had probably washed out a lot of MTBE from the atmosphere). From 9/6/00 - 3/12/01 the median (mean) concentration was 24 ng/L (32 ng/L, not detected – 85 ng/L, n = 35) and 49 % of the data showed a median (mean) concentration of 44 ng/L (53 ng/L,
30 – 85 ng/L, n = 17). Analysis data that were below the detection limit of 10 ng/L were included in the calculations by 10 ng/L throughout the study. The results are compared to daily ambient temperatures and amounts of precipitation (Figures 4-2 and 4-3). Mean values of daily temperatures and precipitation data were produced in the same intervals as the precipitation samples were collected. Thereby, a data point of the MTBE concentration with corresponding temperature and precipitation values represents a mean value of the interval from the date of the point to the former data point.

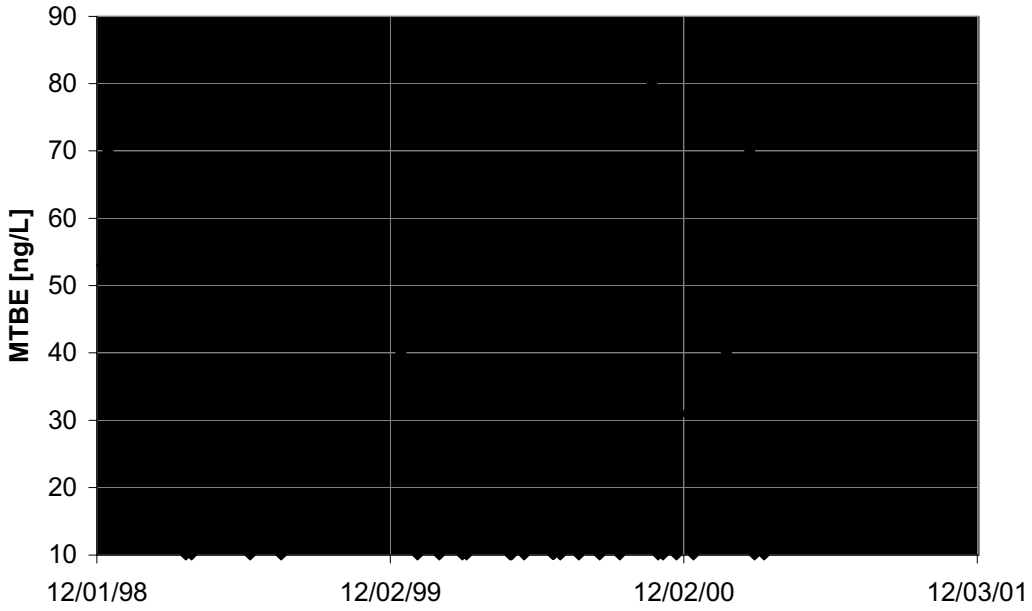


Figure 4-1 Methyl tert-butyl ether (MTBE) concentrations (ng/L) in precipitation in Frankfurt/ M city 1998 - 2001. The average standard deviation for sample analysis is 11 % and the method detection limit 10 ng/L.

Two general observations can be made:

?? The detection of MTBE in urban precipitation is observed at ambient temperatures lower than about 10 - 15 °C.

MTBE concentrations up to 40 ng/L and up to 85 ng/L occurred after the summertime when the ambient temperature was first lower than 15 °C (09/06/00, 09/20/00, 10/12/00, 10/19/00) and 10 °C (10/23/00, 11/01/00, 11/13/00), respectively. Also, at a sudden temperature drop from 10 °C to 1 °C (12/22/00) and remaining temperatures lower than 5 °C for 12 days continuously increasing MTBE concentrations up to 75 ng/L are observed. In February, also at temperature drops from 12.5 °C (02/07/01) to 7.1 °C (02/13/01) and to 4.9 °C (02/22/01) significant MTBE concentrations of 74 ng/L (02/13/01) and 70 ng/L (02/22/01) were detected in precipitation.

?? The first precipitation after a dry period accumulates more MTBE than precipitation during or at the end of a wet period (wash-out effect).

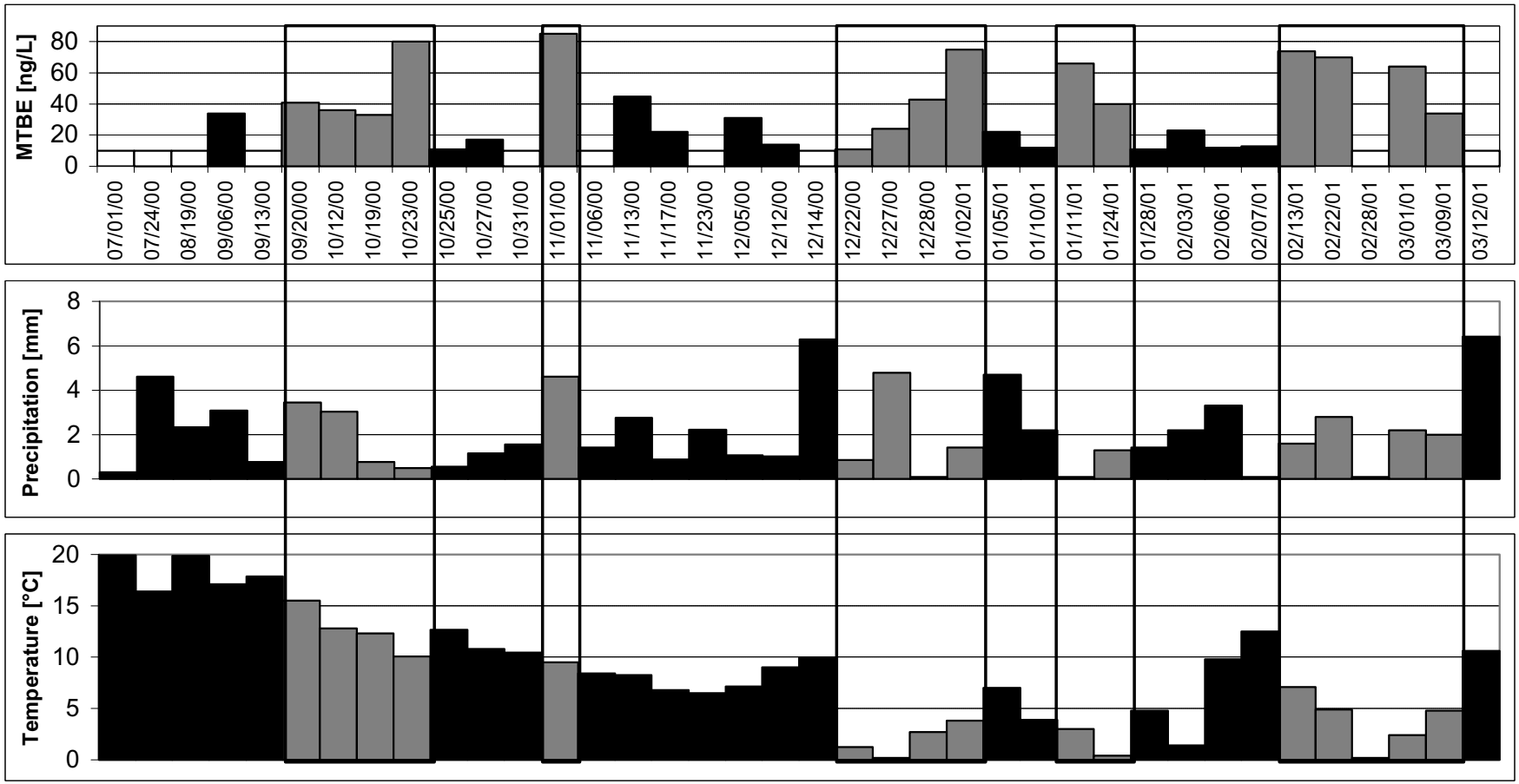


Figure 4-2 Methyl tert-butyl ether (MTBE) concentrations (ng/L) in precipitation in Frankfurt/ M city 2000 - 2001 and ambient temperatures and amounts of precipitation at Frankfurt/ M airport. The average standard deviation for sample analysis is 11 % and the method detection limit 10 ng/L. Grey columns indicate intervals at higher measured MTBE concentrations and white columns indicate samples with no detected MTBE.

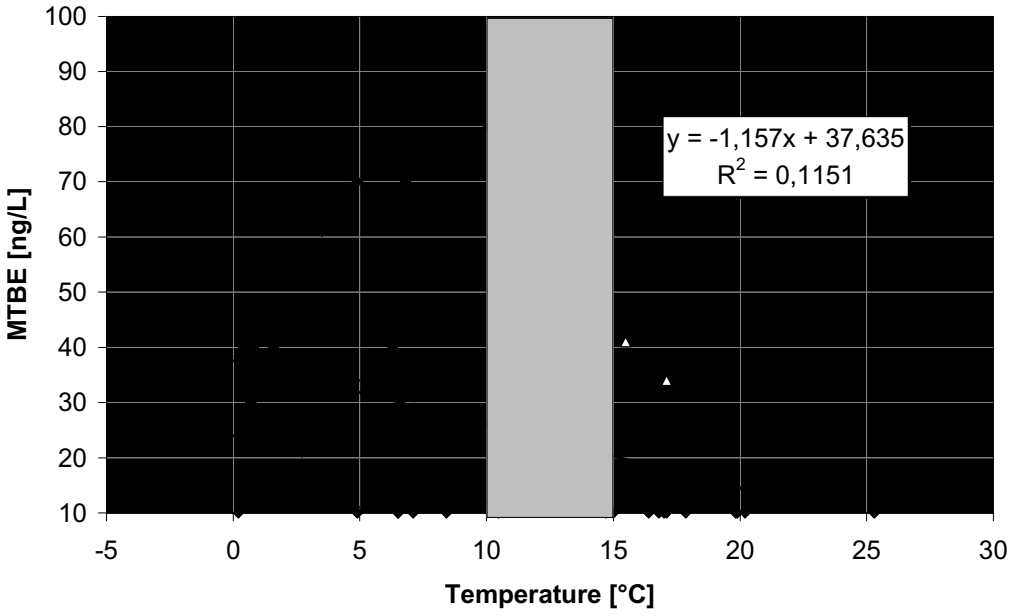


Figure 4-3 Methyl tert-butyl ether (MTBE) concentrations (ng/L) in measured in precipitation in urban areas versus corresponding ambient temperature (°C) from 1998 – 2001 in Germany. Samples that include more than 6 mm precipitation (n = 5) were neglected. Triangles indicate first precipitation samples in autumn after summertime. The average standard deviation for sample analysis is 11 % and the method detection limit 10 ng/L.

The last October week (10/25/00 - 10/31/00) was a dry period (3.5 mm precipitation) that corresponds to practically no detectable MTBE (mean 13 ng/L) which was followed by heavy rain (4.6 mm precipitation) that corresponds to 85 ng/L on the 1st of November. Heavy rain at 12/14/00 might be responsible for a concentration below the detection limit at 12/22/00 although the described temperature drop occurred. Also, at a precipitation amount of more than 6 mm and an ambient temperature of about 10 °C (12/14/00, 03/12/01) MTBE is not detected probably due to significant dissolution. The results might indicate a relation of the MTBE concentration to the interaction of the precipitation amount and the ambient temperature.

In the winter months November 2000, December 2000, January 2001 and February 2001, the comparison of MTBE in urban and rural precipitation was investigated. The results and the corresponding ambient temperatures are shown in Figure 4-4. The cities Bonn, Köln, Hamburg, Stuttgart, Berlin and Frankfurt/ M represent urban areas and sampling locations at Westerland, Zingst, Neuglobsow, Waldhof, Schmücke, Deuselbach, Schauinsland,

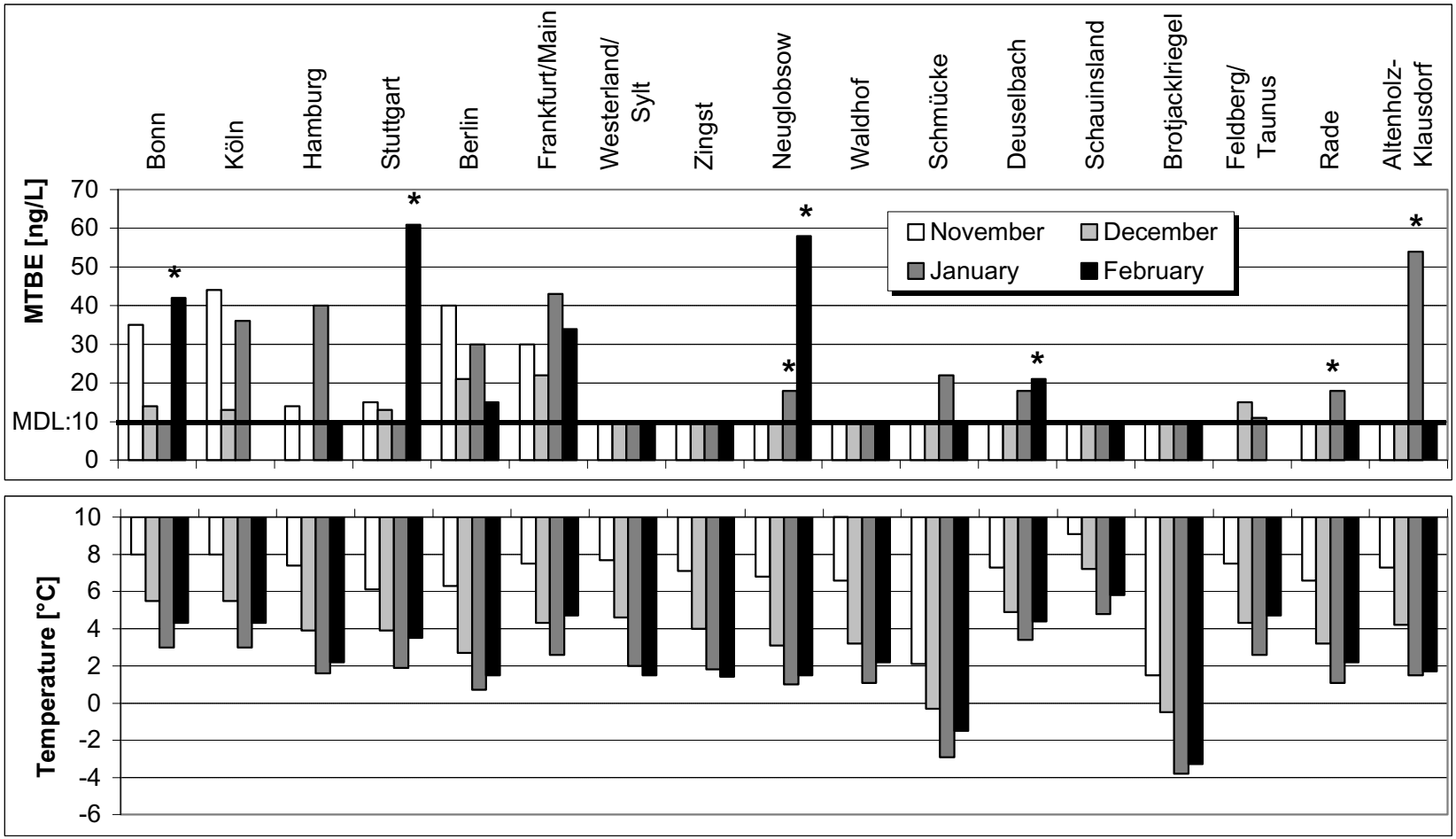


Figure 4-4 Methyl tert-butyl ether (MTBE) concentrations (ng/L) in rural and urban precipitation in Germany in winter 2000/ 2001. Data for Frankfurt/ M and Berlin represent median values. The average standard deviation for sample analysis is 11 % and the method detection limit (MDL) 10 ng/L. Asterics indicate snow samples.

Brotjacklriegel, Rade and Altenholz-Klausdorf are remote or rural areas. MTBE is more often detectable in urban (86 %, n = 78) than in rural precipitation (18 %, n = 42). It has to be taken into account that each data point represents one arbitrary collected spot sample per month and the corresponding temperatures are median monthly values. More than one spot sample per month were collected at Frankfurt/ M (n = 24) and at Berlin (n = 8) only. From the comparison of the Frankfurt/ M and the Berlin data with the data from the other cities it can be concluded that monthly spot sampling provides a too low amount of numbers for an acceptable statistical result because the concentrations fluctuate significantly from one precipitation event to the next one (Figure 4-1). From November/ December 2000 to January/ February 2001 the mean ambient temperature at the investigated locations decreased from 5 °C to 2 °C and simultaneously the average MTBE concentration at all sample locations increased from 15 to 22 ng/L. In this sample set, detection of MTBE was observed at ambient temperatures lower than 8 °C.

The highest MTBE concentrations were detected in snow samples. It is known that snow fall has the potential to significantly collect air pollutants from the atmosphere by washing out the aerosol and sorbing the vapor [WANIA ET AL., 1998; VISKARI ET AL., 1997]. Even at rural locations MTBE was detected in snow samples. Amounts of more than 50 ng/L MTBE in January/ February 2001 at Neuglobsow and Altenholz-Klausdorf may result from the vicinity of the cities Berlin and Kiel.

It is important to notice that in contrast to most parts of the U.S. MTBE is used in Germany at different concentrations in regular, Euro super, super premium unleaded and "Optimax" gasoline. Due to the predominant use of MTBE as an octane enhancer, about the same concentrations are used the year round in Germany whereas in the U.S. the MTBE contents are often increased in the wintertime. The MTBE content in gasoline during wintertime might even be slightly lower due to increased use of butane which is less expensive [PAHLKE ET AL., 2000]. Detectable MTBE concentrations in precipitation in Germany in the wintertime but not in the summertime show that observed higher aqueous detection frequencies in the U.S. in the wintertime [DELZER ET AL., 1996; REISER AND O‘ BRIEN, 1998] are not only the result of the increased use of MTBE but also of its persistent behavior in the atmosphere at low ambient temperatures. In New Jersey, where about 11 % ofMTBE is used the year round,summer and winter concentrations of MTBE have medians of 60 ng/L and 420 ng/L, respectively [BAEHR ET AL., 2001].

4.1.4.2 Comparison of the MTBE Concentrations in Precipitation to Other Data

The MTBE data in precipitation received in this study are calculated to corresponding air equilibrium concentrations (Table 4-2), following the procedure used by BAEHR ET AL. [1999 AND 2001] and BENDER ET AL. [2000]. In this study, measured mean (median) MTBE concentrations in precipitation of 14 ng/L (not detected) in rural areas and 30 ng/L (23 ng/L) in urban areas correspond to mean (median) calculated air concentrations of 0.01 ppb_V (not detected) in rural areas and 0.04 ppb_V (0.02 ppb_V) in urban areas. If the data are compared to other concentrations in Table 4-2, it has to be noticed that the samples in this study were taken at lower ambient temperatures compared to the others. If the precipitation concentrations of this study were calculated using ambient temperatures measured in the studies of BAEHR ET AL. [1999] and BENDER ET AL. [2000], the calculated air concentrations would be 2-5 times higher. MTBE concentrations in the air were observed in the range of about 0.1 - 0.5 ppb_V (rather rural areas) and about 0.5 - 2 ppb_V (rather urban areas). Corresponding calculated water equilibrium concentrations of about 40 – 250 ng/L (rather rural areas) and about 250 – 1700 ng/L (rather urban areas) are reported. Mean MTBE concentrations measured in rural (0.28 ppb_V) and urban air (1.04 ppb_V) in Switzerland [BUWAL, 1999] were in the same order and were calculated to corresponding water equilibrium concentrations of 159 ng/L (rural) and 587 ng/L (urban) by the author of this study using published temperature and atmospheric pressure. MTBE air concentrations measured in mega cities in warm climate were also in the same range in Kairo/ Egypt (1.28 ppb_V) but showed significantly higher concentrations in Porto Alegre/ Brazil (0.2 – 17 ppb_V) and Mexico City/ Mexico (40 – 160 ppb_V). However, these data (and also the Swiss data) were received by GC with flame ionization detection measurement that generally can produce false-positive results [HALDEN ET AL., 2001]. Comparing the data of this study to the measurements in New Jersey/ U.S., California/ U.S. and Switzerland, MTBE concentrations in Germany are about one order of a magnitude lower. The difference may not simply be explained by significant variations of MTBE emissions between the three countries because measured mean air concentrations of 0.82 ppb_V in the U.S. and 0.66 ppb_V in Switzerland for urban and rural areas do not differ significantly although the use of MTBE in gasoline in the New Jersey (11 %) is about 5 times higher than in Switzerland (2 - 3 %) [MRASEK, 2000] and Germany (1.35 – 1.71 %) [SCHOLZ, 2001; PAHLKE ET AL., 2000]. Assuming that the different use in the countries is the main reason for varying MTBE concentrations, another possibility to explain the high atmospheric concentrations in Switzerland may be false-positive MTBE concentration measurements. It seems unclear to what extent local urban air with a higher MTBE concentration is mixed by

Table 4-2 Comparison of measured and calculated methyl tert-butyl ether (MTBE) concentrations in precipitation (ng/L) and air (ppb_V) in Germany, Switzerland, New Jersey (U.S.) and California (U.S.).

Sample medium	Number of samples analysed	Number of samples with a detection	Minimum	Mean	Median	Maximum	Sampling time	Sampling area	MTBE concentration in gasoline in the investigated area, [% w/w]	Reference
Air, ppb_V	57	-	0.11[b]	-	0.25	0.48[b]	years	urban + rural	11	BAEHR ET AL., [2001]; SCHOLZ, [2001]
Calculated water equilibrium, ng/l			40	-	90	160				
Calculated water equilibrium, ng/l	-	-	-	-	60	-	summer	urban + rural	11	BAEHR ET AL., [2001]
Calculated water equilibrium, ng/l			-	-	420	-	winter			
Air, ppb_V	38	38	0.16	0.82	0.85	2.1	spring/ summer	urban + rural	11	BENDER ET AL., [2000]; SCHOLZ, [2001]
Calculated water equilibrium, ng/l			30	350	250	1700				
Air, ppb_V	12	-	-	1.04	-	-	-	urban	about 2 - 3 [MRASEK, 2000]	BUWAL, [1999]
Calculated water equilibrium, ng/l			-	587[ad]	-	-				
Air, ppb_V	24	-	-	0.28	-	-	-	rural		
Calculated water equilibrium, ng/l			-	159[ad]	-	-				
Calculated air equilibrium, ppb_V	58	43	n.d.[c]	0.04[a]	0.02[a]	0.15[a]	winter	urban	1.35 - 1.71 [SCHOLZ, 2001, PAHLKE ET AL., 2000]	this study
Precipitation, ng/l			n.d.[c]	30	23	85				
Calculated air equilibrium, ppb_V	42	9	n.d.[c]	0.01[a]	0.00[a]	0.05[a]	winter	rural		
Precipitation, ng/l			n.d.[c]	14	10	58				

[a] Air equilibrium concentrations are calculated after Seinfeld and Pandis (1998) by use of individual temperatures for each calculation (K), atmospheric pressure p = 1.01325 * 10^5 N/m², gas constant R = 8.314 Nm/(mol*K) and Henry's law coefficient H (dimensionless),

[b] Of the middle 50% of all data,

[c] Not detected,

[d] Calculated by author using published temperature (9 °C) and atmospheric pressure (950 hPa).

other air of the upper atmosphere or from remote areas with a lower MTBE content. If for example the studies are compared by assuming a mean MTBE content of 3 % for the U.S. [SCHOLZ, 2001] measured MTBE air concentrations in the U.S. and Switzerland would be comparable. Generally, atmospheric MTBE can be transported for long distances, e.g. throughout Europe [SCHOLZ, 2001] regarding the half-life time of 5.5 days in the atmosphere [RIPPEN, 1994; BENNETT AND KERR, 1990]. This may be even more important in the wintertime, when less hydroxyl radicals are produced. Detectable MTBE concentrations in rural snow samples can thereby be explained. Neglecting all calculations and possibly differing origin of MTBE in air and precipitation, low measured concentrations in precipitation and higher amounts in the air may represent the degradation process in the atmosphere or the photochemical degradation of MTBE in the gas phase and the chemical degradation in the water phase. The wash-out effect will also contribute to different MTBE concentrations in the air and precipitation.
Different urban sampling methods (e.g. distance to road traffic) might also be a reason for varying measured atmospheric MTBE concentrations. Urban air sampling frequently occurred next to a road only a few meters or centimeters above the ground whereas precipitation sampling occurred on the roof of the Institut für Mineralogie –Umweltanalytik at Frankfurt/ M city about 10 m above and 200 m away from direct road traffic.

4.1.4.3 Urban Runoff

Urban runoff samples (n = 12) that were collected on a road 500 m away from precipitation sampling at Frankfurt/ M at the same time showed a wide concentration range from 30 – 1174 ng/L with a median (mean) concentration of 114 ng/L (204 ng/L). Due to the low sample amount, only rough estimations can be made. By comparing MTBE in urban runoff to MTBE in precipitation in the wintertime in Germany, the results indicate that about 20 % of the MTBE in urban runoff may already be transported by precipitation down to a vertical hight of about 10 m above the ground whereas about 80 % may be attributed to direct uptake of vehicle emissions and gasoline on the road. In the U.S. the mean and median water equilibrium concentrations of 90 - 420 ng/L (calculated from air measurement by BENDER ET AL., 2000; BAEHR ET AL., 1999 AND 2001) represent about 5 – 30 % of the mean stormwater concentration of 1500 ng/L (200 – 8700 ng/L, n = 592), [LOPES AND BENDER, 1998; DELZER ET AL., 1996].

4.1.5 Conclusions

The results of this study show the presence of MTBE in urban and rural precipitation in Germany in wintertimes. In urban precipitation, MTBE is observed at ambient temperatures lower than about 10 - 15 °C whereas highest concentrations are detected in snow samples. Wash-out mechanisms known from other organic compounds are observed. Due to the year round use of MTBE in Germany a persistent behavior in the atmosphere in wintertimes that leads to detectable concentrations in precipitation can be concluded. MTBE concentrations in Germany in the wintertime are about one order of a magnitude lower than year round and summertime measurements in the U.S. and in Switzerland. Possibilities to explain the difference include a wide variety of assumptions. It cannot be clarified whether the different use of the ether in gasoline in the countries, analytical uncertainty, atmospheric degradation processes or a combination of all are responsible. More research is needed in this field. The comparison of MTBE concentrations in precipitation and urban runoff have shown that about 20 % of the MTBE detected in urban runoff is already transported in the atmosphere before precipitation whereas about 80 % may be attributed to direct uptake of vehicle emissions and gasoline on road.

4.2 MTBE in River and Waste Water

4.2.1 Abstract

An overview of methyl tert-butyl ether (MTBE) concentrations in German river water (315 samples) and waste water (82 samples) is given. In the agglomerated area of Frankfurt/ M, several samples of surface water, waste water and industrial effluents were analyzed for its MTBE content from 1999 to 2001. MTBE was analyzed by a combination of headspace-solid-phase microextraction and gas chromatography/ mass spectrometry (HS-SPME/ GC-MS). Rhine and Main water concentrations of MTBE in the lower parts of the rivers were approximately 250 ng/l and 200 ng/L, respectively. The concentrations increased from the upper parts of the rivers to its mouths. Water from the Elbe, Neckar and Weser rivers showed lower MTBE concentrations and the ether was not detected in the Danube river. Generally, higher MTBE concentrations were detected at urban agglomerations compared to rural areas. Small urban creeks without significant industrial input showed MTBE concentrations of approximately 50 ng/L and it was hardly detectable in small rural creeks. Higher MTBE

concentrations in river water were correlated with increased concentrations of the oxygenate measured in precipitation. The analyzed river water samples showed a tendency towards increasing concentrations from 1999 to 2001. Most MTBE concentrations in river water fell in the range of 50 – 200 ng/L (32 %), 10 – 50 ng/L (28 %) and 200 – 1000 ng/L (26 %). MTBE concentrations in German surface water and air are 2 – 17 times lower compared to Californian data. Waste water samples from influents of two sewage plants showed MTBE concentrations of approximately 100 – 300 ng/L and a loading of 2 – 37 kg/a was calculated. Industrially influenced samples of river water or public waste water and industrial effluents showed MTBE concentrations up to 2267 ng/L and 28 µg/L, respectively. This input has not been considered before because only 1.5 % of the produced amount of MTBE in Germany is used for industrial processes but it should not be neglected because MTBE is very persistent in water.

4.2.2 Introduction

In the last years, the intensive use of the oxygenate methyl tert-butyl ether (MTBE) has led to major concern about its distribution in the aquatic environment and its occurrence in drinking water resources in the U.S. [CLAWGES ET AL., 2001]. In Germany, authorities only recently began to evaluate the MTBE situation in the country [PAHLKE ET AL., 2000] and decided not to implement a drinking water and surface water standard because MTBE concentrations in Germany are believed to be generally low. Other reasons for the decision were the presence of significantly lower MTBE concentrations in german gasoline compared to some U.S. states, decreasing MTBE emissions from automobiles and handling of MTBE by improved technology, such as use of double-sided tanks at gasoline stations from 1992 to 1998. Additionally, the WORLD HEALTH ORGANIZATION's conclusion in 1998 that acute health risks for the public are unlikely [WHO, 1998] was used as an argument. The Umweltbundesamt estimated a reduction of MTBE emissions in Germany from approximately 6000 t/a in 1992 to approximately 2200 t/a in 1999. However, monitoring of the oxygenate particularly at sites contaminated with gasoline has been intensified by the Umweltbundesamt [PAHLKE ET AL., 2000] because concentrations are generally higher at these sites.

An elevation in MTBE emissions due to increasing concentrations in gasoline since 1992/ 1993 and a greater number of registered cars in the country from 1994 (39 mio) to 2001 (44 mio) [STATISTISCHES BUNDESAMT, 2001] can be expected. It seems unclear if the effect of reduced MTBE emissions from automobiles and improved handling of gasoline dominates,

compensates for or secondarily influences the effect of the increasing use of the oxygenate. In 2005, a new guideline will be introduced by the European Union limiting the amount of aromatic compounds in gasoline to 35% (v/v). It is not yet clear however how the required octane values will then be reached.

MTBE is emitted by different sources into the aquatic environment. Due to its solubility and persistence in water, it is diluted by large amounts of surface and ground water and can be transported over long distances [PANKOW ET AL., 1996] without needing to be adsorbed to particles. Leakage from underground storage tanks (LUST's) at high concentrations into groundwater represents the most important pathway in terms of its introduction to the environment [WEAVER ET AL., 1996; BORDEN ET AL., 1997; BUXTON ET AL., 1997; DALY AND LINDSEY, 1997; GRADY, 1998; LANDMEYER ET AL., 1998;, ZOGORSKI ET AL., 1998; MACE ET AL., 1998; SCHIRMER AND BARKER, 1998; LINCE ET AL., 1998 AND 2001; MORAN ET AL., 1999; HATTEN AND BLACKBURN, 1999; HAPPEL ET AL., 1999, JOHNSON ET AL., 2000; KOLB 2000; EFFENBERGER ET AL., 2001]. Recreational watercraft is another known emission source that causes MTBE contamination in the upper water zones of lakes in the summertime when its use is highest [BAEHR AND ZAPECZA, 1998; BOUGHTON AND LICO, 1998; REUTER ET AL., 1998; BROWN ET AL., 2001]. Studies of two-stroke engines showed that up to 30 % of unburnded fuel is discharged into the environment [ARB, 1999]. Industrial effluents represent another point source for MTBE in river water. In Southern California, highest MTBE concentrations (up to 1878 µg/L) were observed in effluents from refineries [BROWN ET AL., 2001]. However, discharges from public sewage plants accounted for 78 % of the daily mass emission of MTBE. For Santa Monica, a load of 78 t/a of MTBE from all industrial effluents was calculated. Its presence in effluents has in fact been reported by the chemical industry. In Germany, for example, one chemical company reported emitting a total of 1.9 t of MTBE into the Rhine river in 1998 [BASF, 1999].

The occurrence of MTBE in the hydrological cycle and its impact as a non-point source contaminant has been investigated in several studies [DELZER ET AL., 1996; PANKOW ET AL., 1997; LOPES AND BENDER, 1998; REISER AND O'BRIEN, 1998, BRAUCH ET AL., 2000A, EFFENBERGER ET AL., 2001, BENDER ET AL., 2000; BAEHR ET AL., 1999 AND 2001; ACHTEN AND PÜTTMANN, 2000; ACHTEN ET AL., 2001A AND 2002B, CLAWGES ET AL., 2000]. The detection of MTBE in urban runoff [DELZER ET AL., 1996; LOPES AND BENDER, 1998] first indicated that parts of the oxygenate added to gasoline and used by automobiles is transported from the gaseous phase from exhausts into the aqueous phase during precipitation events. MTBE measurement in air samples taken in a tunnel in Los Angeles showed that 155 mg of

MTBE per used liter of gasoline (containing 10 % MTBE) was emitted into the atmosphere [FRASER ET AL., 1998]. Automobile exhaust gases represent a major source of MTBE in ambient air [MEF, 2001]. Urban runoff mixed with domestic and industrial waste water is often collected by sewage plants before it is released into the rivers. MTBE may pose a significant wastewater treatment problem [MEF, 2001] but data are rather scarce. A single concentration of 910 ng/L MTBE was measured in Helsinki (Finland) in a wastewater sample from an urban sewer network that collected mixed emissions from MTBE. Discharges from European MTBE producing industries ranged from not detected to 1000 µg/L use [MEF, 2001]. In New Jersey, U.S., non-point sources were assumed to be responsible for the detections of MTBE in river water because the concentrations were lower compared to groundwater and could not be explained by a single emission source [REISER AND O'BRIEN. 1998]. The atmospheric transport of low concentrations of MTBE into surface water represent a possible non-point source [PANKOW ET AL., 1997; BAEHR ET AL., 1999 AND 2001]. The existence of this pathway was confirmed by positive correlations between measured river water concentrations (without industrial input) and calculated aqueous concentrations that were in equilibrium with measured MTBE concentrations in the air near the river [BENDER ET AL., 2000]. In Germany, only a few studies have investigated the occurrence of the oxygenate in river and lake water and average concentrations were mostly in the range of 100 – 250 ng/L in 1999/ 2000 [BRAUCH ET AL, 2000A, ACHTEN AND PÜTTMANN, 2000; EFFENBERGER ET AL., 2001; MEF, 2001]. Average MTBE concentrations from 420 – 480 ng/L in two Finish urban creeks and a single sample of 193 ng/L MTBE in water from the Vantaanjoki river downstream of Helsinki were reported (Finish gasoline is oxygenated by 8.5 – 9.2 % MTBE [MEF, 2001; PAHLKE ET AL., 2000]). In Italy (2.9 % MTBE in gasoline), concentrations of the oxygenate in water from the Reno and Setta rivers were 100 – 150 ng/L [PIAZZA ET AL., 2001]. In the Netherlands (1.6 – 2.4 % MTBE in gasoline [MEF, 2001; PAHLKE ET AL., 2000]), 1500 – 7000 ng/L for the Rhine, Meuse, Northern Delta Area and Westerscheldt were reported [MIERMANNS ET AL., 2000]. Concentrations ranging from not detectable to 590 ng/L were found in Danish lakes (0.2 – 3.1 % MTBE in Danish gasoline) and 390 – 6130 ng/L in sea water of boat harbours in Helsinki [MEF, 2001; PAHLKE ET AL., 2000]. MTBE was also detected in german urban and rural precipitation in wintertime [ACHTEN ET AL., 2001A]. In this study, snow samples often contained higher concentrations compared to rain water samples. The occurrence of the oxygenate even at rural sites confirms that MTBE can be transported over long distances in the atmosphere [SCHOLZ, 2001]. Snow samples collected

from heaps near a busy road showed high MTBE concentrations of 720 – 7030 ng/L in Italy [PIAZZA ET AL., 2001].

In the U.S., the impact of MTBE concentrations in groundwater and surface water on drinking water quality is subject of many environmental studies. In Germany, extensive data of MTBE concentrations in the aquatic and atmospheric environment are not available. The lack of data is responsible for different evaluations of the environmental and human health impacts of MTBE in Germany [SCHOLZ, 2001; PAHLKE ET AL., 2000]. The primary objective of this study is to give an overview of MTBE concentrations in German surface waters. Secondary objectives are to identify emission sources of different source strengths and to recognize a possible trend in the development of the MTBE concentrations over time. In this study, MTBE concentrations in water samples of rivers and rural creeks in Germany, and rivers, urban creeks (with and without industrial input), domestic and industrial waste water in the agglomerated area of Frankfurt/ M were observed. To our knowledge, this is the first report on a detailed distribution of aquatic MTBE in an agglomerated area in Germany.

4.2.3 Waste Water Processing at Sewage Plants Frankfurt/ M-Niederrad and Sindlingen

Specifically, waste water samples were collected from two sewage plants (Frankfurt/ M-Niederrad and Sindlingen) in wintertime 2000/ 2001. Sampling and analyses are detailled in the following sections. The processing of waste water at the sewage plants Frankfurt/ M-Niederrad and Sindlingen are similar and include three clarification and two biological steps. Raw water is pumped through rakes and coarse solid material is separated mechanically from the water. The water is then transported into a sand trap where the first sedimentation process occurs. In the first clarification basin (pre-clarification), sludge partitions from water and present organisms can degrade pollutants. The pre-clarification is followed by the first biological step. In this basin, air is bubbled into the water that stimulates particularly heterotrophic bacteria. During the aerobic process, most pollutants are eliminated due to biological activity and volatilization. During the second (intermediate) clarification process, sedimented sludge is pumped partially into the basin of the first biological step for improved biological activity in the basin. During the second biological step, microbial activity is stimulated by introduced sludge from the following third (post) clairfication step and the addition of air. After the post clarification process and a mean residence time in the sewage plant of about 12 h, the water is pumped into river water.

4.2.4 Sampling

River water samples were collected by single-point grab sampling at a depth of about 30 cm below the surface of the water from 05/26/99 - 03/01/01. The samples were collected by using different procedures. For the investigation of the spatial distribution of MTBE in German rivers, spot sampling was performed at the Rhine (11/06/00 and 11/07/00) from Schaffhausen to Wesel, at the Elbe (09/02/00) from Boitzenburg to Glücksstadt and at the Main (05/17/00 and 08/30/00) from Offenbach to the mouth (into the Rhine) at Gustavsburg. Samples from the Main river at Frankfurt/ M city, Frankfurt/ M-Nied and close to Bischofsheim, from the Rhine river close to Wiesbaden/ Mainz and from urban creeks in the vicinity of Frankfurt/ M were collected over time to study the temporal development of the MTBE concentrations. Water samples taken from the Main river close to Bischofsheim represent mixed samples collected over a period of 24 h. Rhine water samples close to Wiesbaden/ Mainz were collected from the bottom of the river. Three sample sets of Rhine (09/06/00) and Main river water (09/19/00 – 09/22/00, 01/16/01 – 01/18/01) were collected during voyages on the ship Argus that is regularly used for research purposes by the HESSISCHE LANDESANSTALT FÜR UMWELT (HLUG). For this purpose, the speed of the ship is reduced to equal the river water velocity and samples are collected every 5 – 15 km. By travelling within a water body sudden changes of characteristic water parameters may indicate for example a local industial input from a pipe or significant inflow from other water. Waste water samples from sewage plants and industrial effluents were collected over a period of 24 h and 2 h, respectively, for the investigation of possible emission sources. Effluents from the Niederrad sewage plant from 11/11/00 - 02/05/01 were however sampled using a single-point grab method.
The water samples were stored in 100 ml sample vials that were acidified before by addition of concentrated (33%) hydrochloric acid. After the bottles were completely filled with no headspace left they were cooled to 4 °C and analysed within 3 weeks after collection.

4.2.5 Results

4.2.5.1 MTBE in German River Water

For the investigation of the spatial distribution of MTBE in German rivers, spot sampling was performed at the Rhine (11/06/00 and 11/07/00) from Schaffhausen to Wesel (Figure 4-5), at the Elbe from Boitzenburg to Glücksstadt (Figure 4-6) and at the Main from Offenbach to the mouth (into the Rhine) at Gustavsburg. The median MTBE concentration determined in

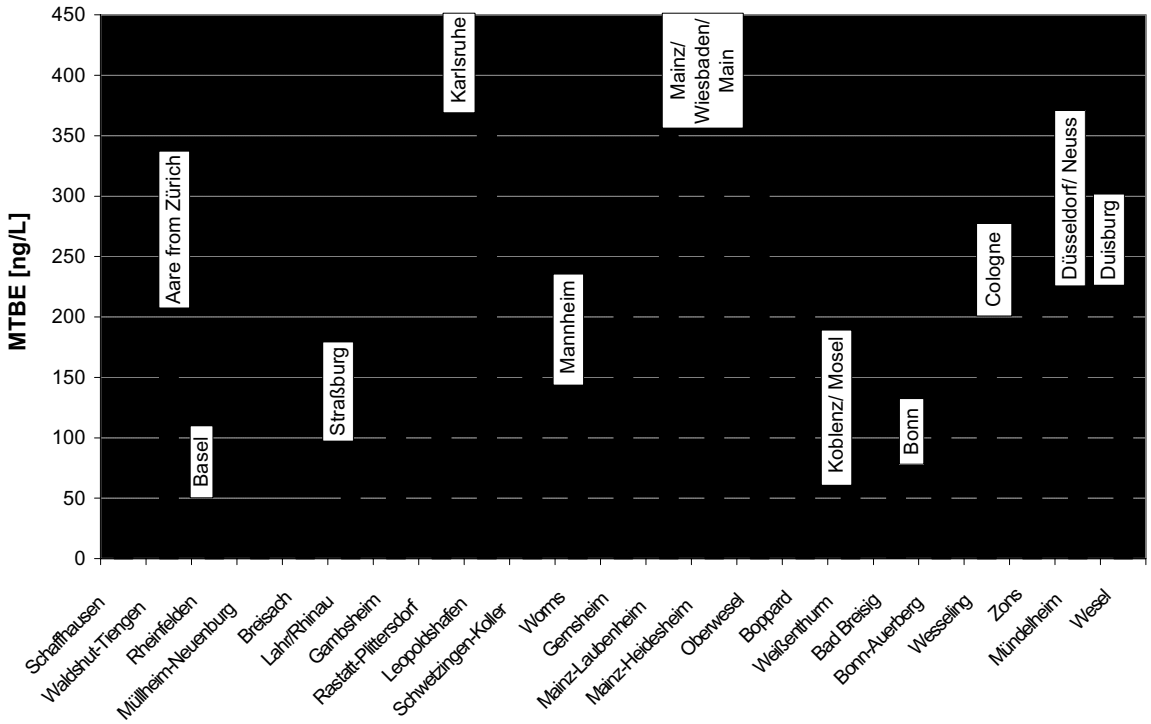


Figure 4-5 Methyl tert-butyl ether(MTBE) concentrations (ng/L) in Rhine water from Schaffhausen to Wesel on the 11/06/00 – 11/07/00. Samples were collected by spot sampling. The detection limit of the method was 10 ng/L with a relative standard deviation of 11 %.

Rhine water increased from the lower part of the Rhine (from Schaffhausen to Rastatt) with a value of 69 ng/L, to the upper part (from Karlsruhe to Wesel), where a concentration of 216 ng/L was measured. Median MTBE concentrations in the Elbe and Main were 31 ng/L and 340 ng/L, respectively. Higher MTBE concentrations were observed near urban agglomerations (Frankfurt/ M, Karlsruhe, Mainz, Köln, Düsseldorf, Duisburg, Hamburg) compared to lower amounts found at rural areas (Schaffhausen, Rheinfelden, Müllheim, Breisach, Weißenthurm, Bad Breisig, Boitzenburg, Lauenburg, Tesperhude, Geesthacht, Winsen and Meckelfeld-Over). From 05/11/00 - 01/08/01, Rhine water samples collected at Wiesbaden/ Mainz showed a median concentration of 301 ng/L (Table 4-3), corresponding to a loading of about 15 t/a in 2000/ 2001 at a flow of 1600 m^3/s. The median concentration of all Rhine water samples measured from Karlsruhe to Wesel was 254 ng/L.
Main water samples collected at Frankfurt/ M city over a period of about 2 years (Figure 4-7) allow for the observation of the temporal distribution of MTBE. Between May 1999 and April 2000, the median MTBE concentration was 32 ng/L. The concentration increased to 114 ng/L

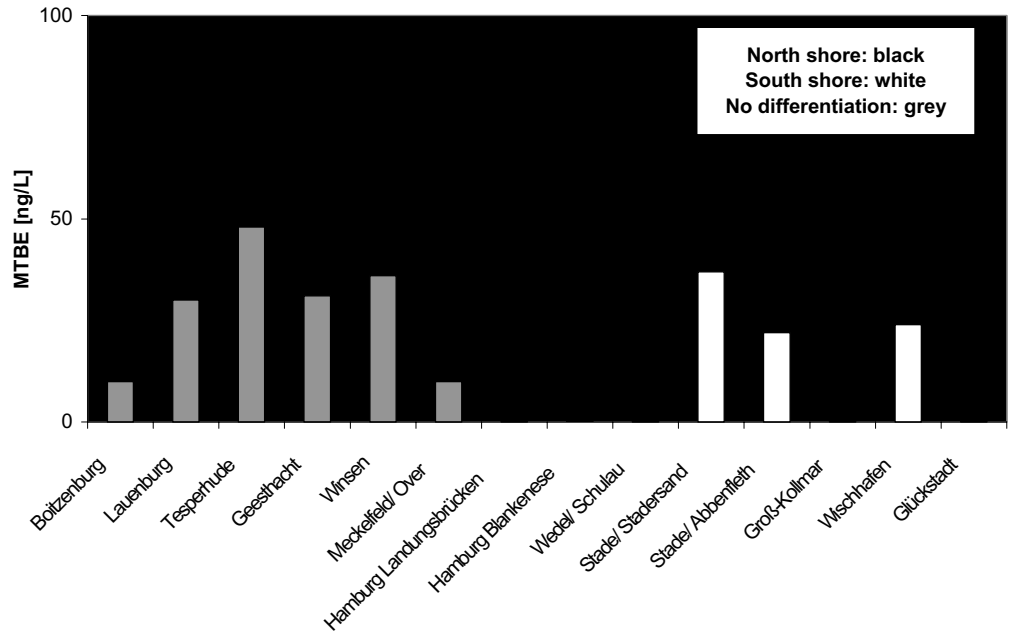


Figure 4-6 Methyl tert-butyl ether (MTBE) concentrations (ng/L) in Elbe water from Boitzenburg to Glückstadt on the 09/02/00. Samples were collected by spot sampling. The detection limit of the method was 10 ng/L with a relative standard deviation of 11 %.

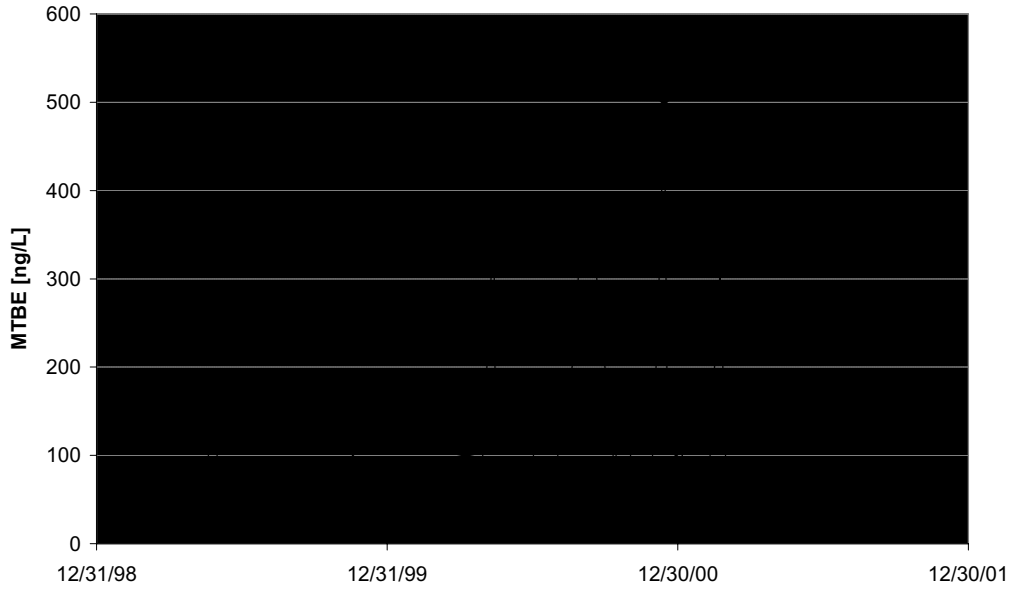


Figure 4-7 Methyl tert-butyl ether (MTBE) concentrations (ng/L) in Main water at Frankfurt/ M city from 1999 – 2001. Samples were collected by spot sampling. The detection limit of the method was 10 ng/L with a relative standard deviation of 11 %.

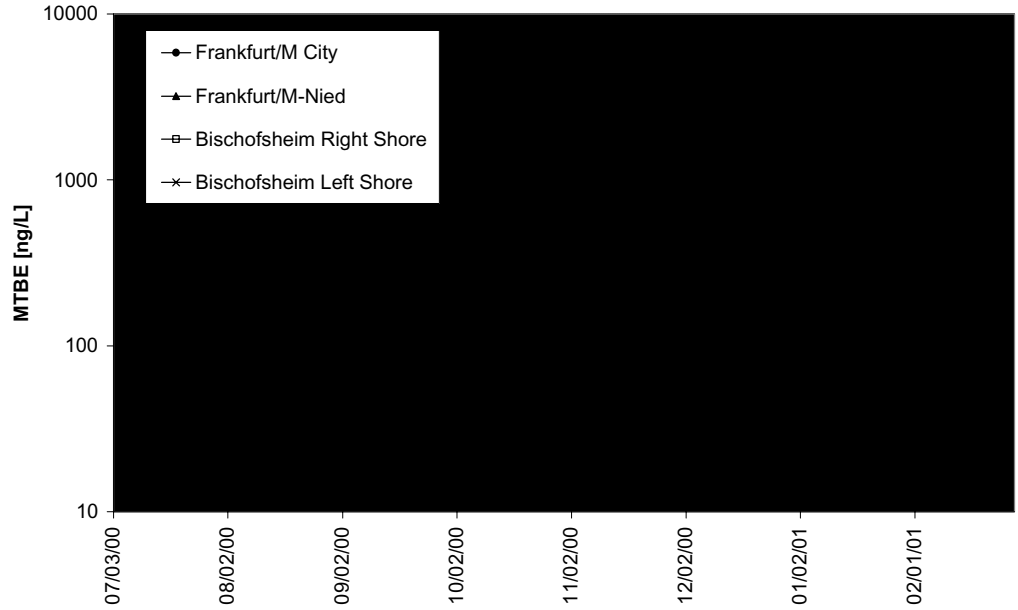


Figure 4-8 Methyl tert-butyl ether (MTBE) concentrations (ng/L) in Main water at Frankfurt/ M city, Frankfurt/ M-Nied, and Bischofsheim (right and left shore) from 07/13/00 – 02/21/01. Samples at Frankfurt/ M were collected by spot sampling and at Bischofsheim over a period of 24 h. The detection limit of the method was 10 ng/L with a relative standard deviation of 11 %.

from May 2000 to March 2001 which corresponds to a loading of about 0.7 t/a in 2000/ 2001 at a flow of 190 m^3/s. Three different Main water sampling locations at Frankfurt/ M city, Frankfurt/ M – Nied and Bischofsheim (left and right shore) near the mouth of the Main into the Rhine were investigated from 07/13/00 - 02/21/01 (Figure 4-8). Observed MTBE concentrations at the different locations are often similar for the same sampling date. For these Main water samples, a median concentration of 116 ng/L and a mean of 196 ng/L resulted. Since December 2000, significant industrial input of up to 2357 ng/L at Frankfurt/ M–Nied was detected. The median Main water concentrations of all samples collected in the upper Main at Seligenstadt was 23 ng/L compared to 111 ng/L (mean of 186 ng/L) in the lower part from Offenbach to Gustavsburg. At Bischofsheim, the median concentration was 184 ng/L, which corresponds to a loading of about 1.5 t/a in 2000 and 2001 at a flow of 250 m^3/s. At Bischofsheim, no significantly increased MTBE concentrations from 1999 to 2001 can be observed. MTBE concentrations in Elbe water are lower, often falling below 50 ng/L. At Hamburg city, at the spot sampling within a day, a median concentration of

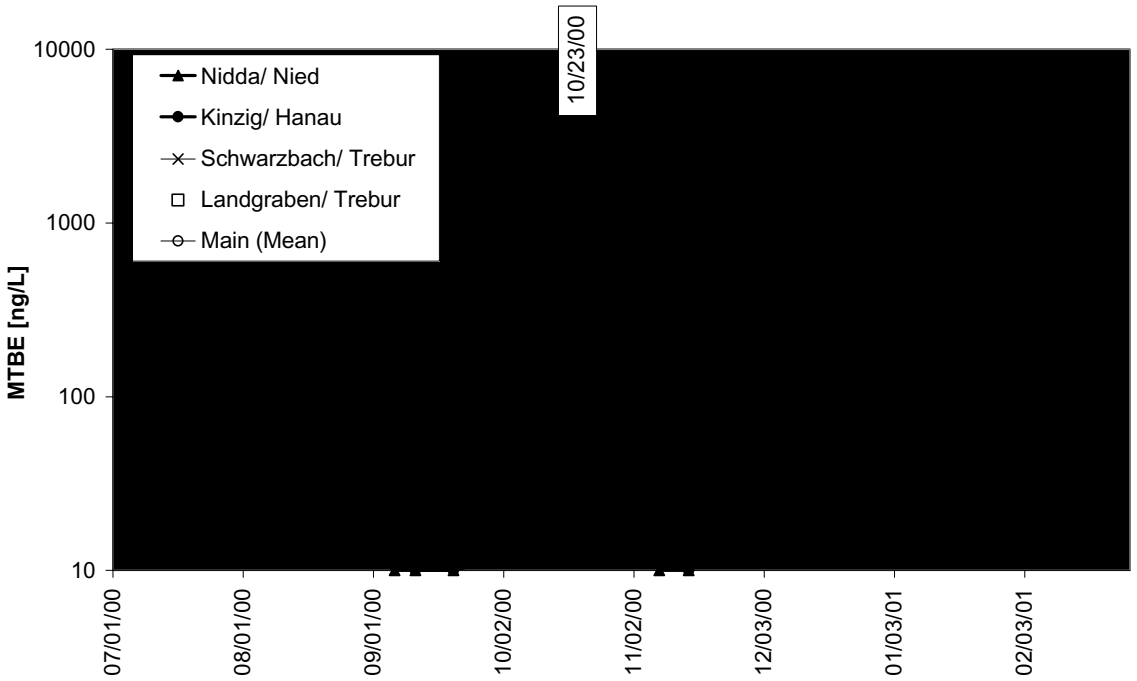


Figure 4-9 Methyl tert-butyl ether (MTBE) concentrations (ng/L) in water from small urban creeks and from the Main river (mean) from 12/07/00 – 02/21/01. Samples were collected by spot sampling. The detection limit of the method was 10 ng/L with a relative standard deviation of 11 %.

82 ng/L was observed. From 04/22/99 - 02/14/01 the median concentration at Hamburg city was 59 ng/L. MTBE is not detected in any water sample of the Danube river in the South of Germany, but in Weser water in the North of the country, in the range of 126 – 162 ng/L. From 07/12/00 - 02/21/01, MTBE was also detected in small creeks in the vicinity of Frankfurt/ M (Figure 4-9). Median concentrations in water from the Schwarzbach of 155 ng/L, Landgraben of 1183 ng/L, Nidda of 25 ng/L and Kinzig of 32 ng/L are calculated. For comparison, the mean Main water concentration is shown. The annual MTBE loading in 2000/ 2001 for the Nidda at Nied and Kinzig at Hanau were about 150 kg/a each at flows of 10 – 11 m^3/s. In all rivers, exceptionally high concentrations were observed on 10/23/00. The temporal distribution of the MTBE concentrations in the different creeks sometimes correlate. Good correlation is observed by comparing of the Nidda and Kinzig rivers that are mainly free of industial input. In Lahn water, the MTBE concentrations show a median concentration of 43 ng/L which increase from the source to the mouth (Figure 4-10). However, no

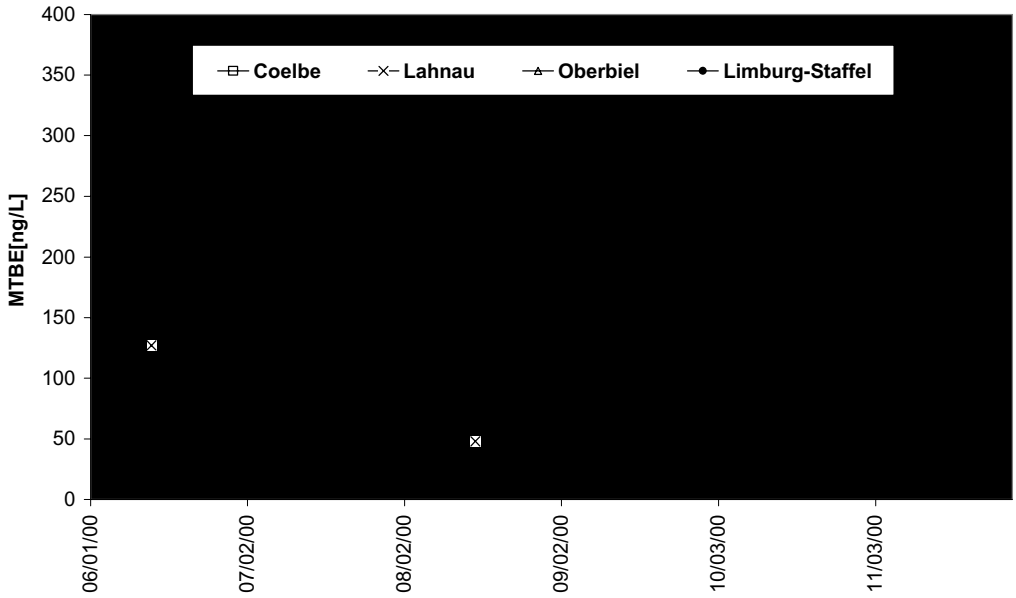


Figure 4-10 Methyl tert-butyl ether (MTBE) concentrations (ng/L) in water from Lahn creek 12/07/00 – 02/21/01. Samples were collected by spot sampling. The detection limit of the method was 10 ng/L with a relative standard deviation of 11 %.

maximum value is observed at the 10/23/00 and from August to November 2000 the concentrations do not increase as observed for other river water. Water samples from channels and nearby rivers were investigated at four locations. In Germany, channels are often located near natural rivers, and due to higher ship's traffic and lower river water velocities caused by locks, it had been assumed that water from channels would have higher MTBE concentrations compared to near river water. MTBE concentrations in water samples of the Mittellandkanal (204 ng/L) and the Weser (162 ng/L) at Bremen, of the Elbe-Lübeck-Kanal (55 ng/L) and the Elbe (30 ng/l) at Lauenburg and of the Grand Canal D'Alsace (127 ng/L) and the Rhine (13 ng/L) at Müllheim confirm this assumption. 736 ng/L was measured in Lippe water compared to 28 ng/L in water from the Wesel-Datteln-Kanal at Wesel (11/06/00). The results of the analysis of 38 small creek water samples in Germany show only low concentrations with a median of 12 ng/L.

Detection frequencies of all measured samples are shown in Figure 4-11. The highest numbers of MTBE concentrations in all river water samples (n = 315) were detected in the ranges from 50 – 200 ng/L (32 %), 10 – 50 ng/L (28 %) and 200 – 1000 ng/L (26 %). In Main

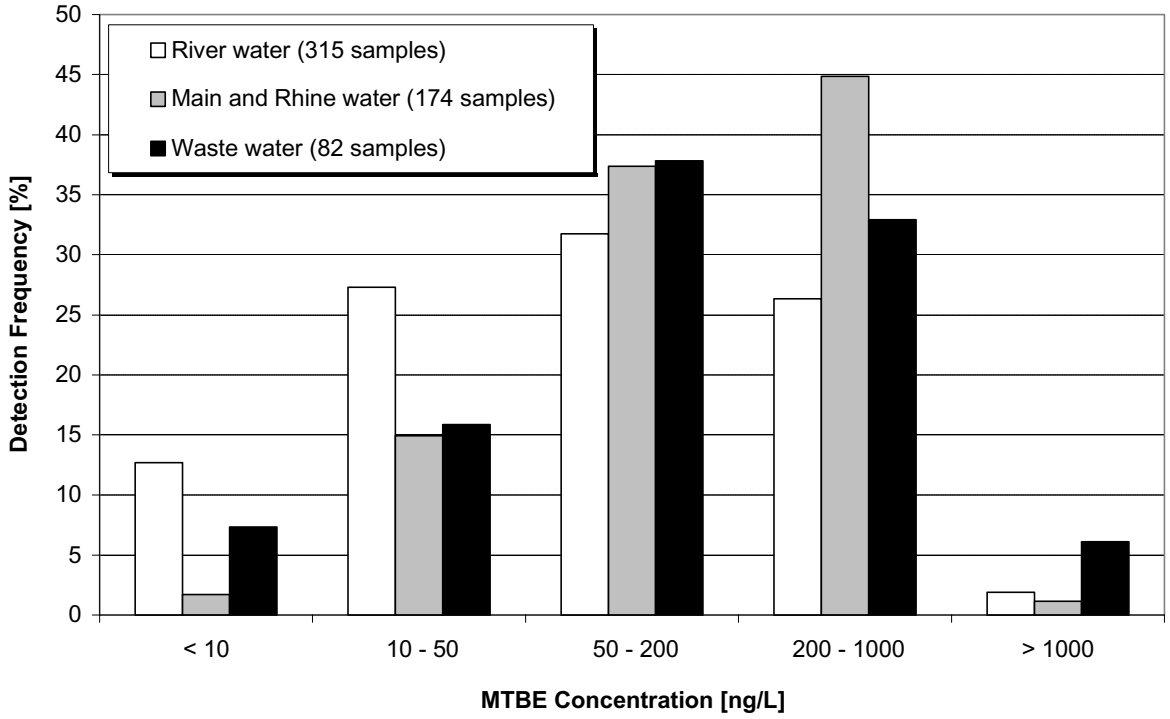


Figure 4-11 Detection frequencies of methyl tert-butyl ether (MTBE) concentrations (ng/L) in surface water and waste water in Germany from 1999 – 2001. The detection limit of the method was 10 ng/L with a relative standard deviation of 11 %.

and Rhine water (n = 174), 45 % of the data fell in the range of 200 – 1000 ng/L and 37 % in the range of 50 – 200 ng/L.

Recently, MTBE has been reported to commonly co-occur with trihalomethanes and solvents but not typical compounds of gasoline like BTEX in groundwater in the U.S. [CLAWGES ET AL., 2000, GARABEDIAN ET AL., 1998]. Chloroform (CF), trichloroethene (TCE) and tetrachloroethene (PCE) are also detected by the analytical method used in this study (Figure 4-12). The detected CF, TCE and PCE concentrations could only be roughly evaluated incomparison to the MTBE amounts in the same samples. BTEX compounds were not investigated in this study. The results show that the chlorinated compounds were always present in the samples with a few exceptions only. No absolute concentrations are given here due to the analytical procedure but the relative ranking of the compounds with respect to detected amounts from the largest to the lowest is CF, MTBE, PCE and TCE. The same ranking was reported by the U.S. studies [CLAWGES ET AL., 2000, GARABEDIAN ET AL., 1998].

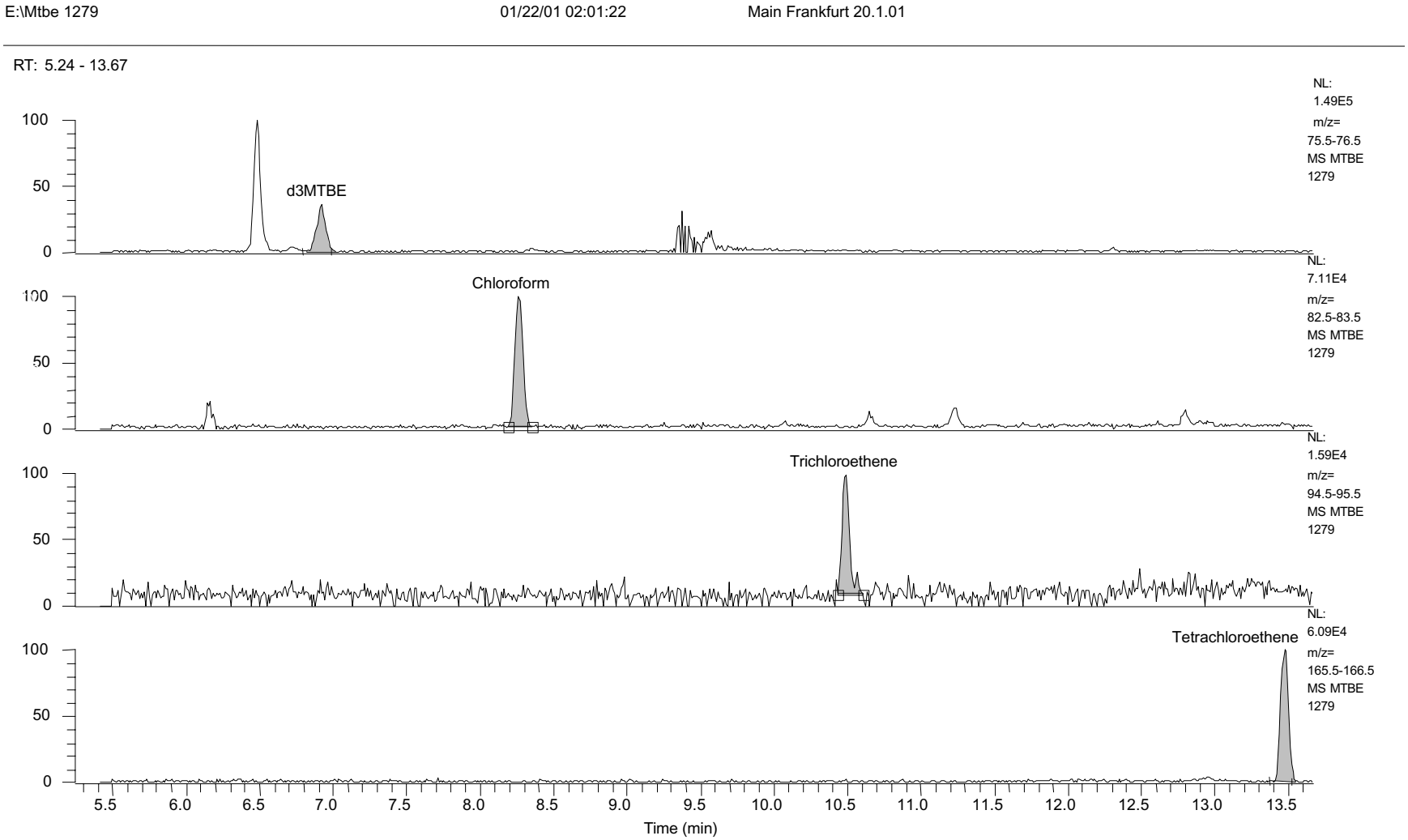


Figure 4-12 Mass chromatography of trichloromethane (chloroform, CF), trichloroethene (TCE), tetrachloroethene (PCE) and internal standard d_3MTBE in water from the Main river at Frankfurt/ M by use of the described method .

4.2.5.2 MTBE in Domestic and Industrial Waste Water

Waste water influents and effluents of two sewage plants at Frankfurt/ M-Niederrad and Sindlingen (Figure 4-13) and effluents of companies in the vicinity of Frankfurt/ M were investigated from 06/13/00 - 03/01/01 (n = 82). The influent „Griesheim“, „Niederrad“ and the effluent of the sewage plant Niederrad show median (mean) concentrations of 196 ng/L (214 ng/L), 299 ng/L (384 ng/L) and 78 ng/L (265 ng/L) of MTBE, respectively. The influent „Niederrad“, which collects mostly industrial sewage is characterized by some exceptional high MTBE concentrations up to 1268 ng/L (12/28/00). From the sewage plant Niederrad a MTBE loading of 10 – 37 kg/a was calculated. The median (mean) MTBE concentrations of 96 ng/L (165 ng/L) for waste water influent and of 81 ng/L (164 ng/L) for effluents of the sewage plant Sindlingen were measured and a loading of 2 – 5 kg/a is calculated. The median (mean) MTBE concentrations in domestic waste water (influent „Griesheim“ of sewage plant Niederrad and influent of sewage plant Sindlingen) increases from 49 ng/L (66 ng/L, 11/11/00

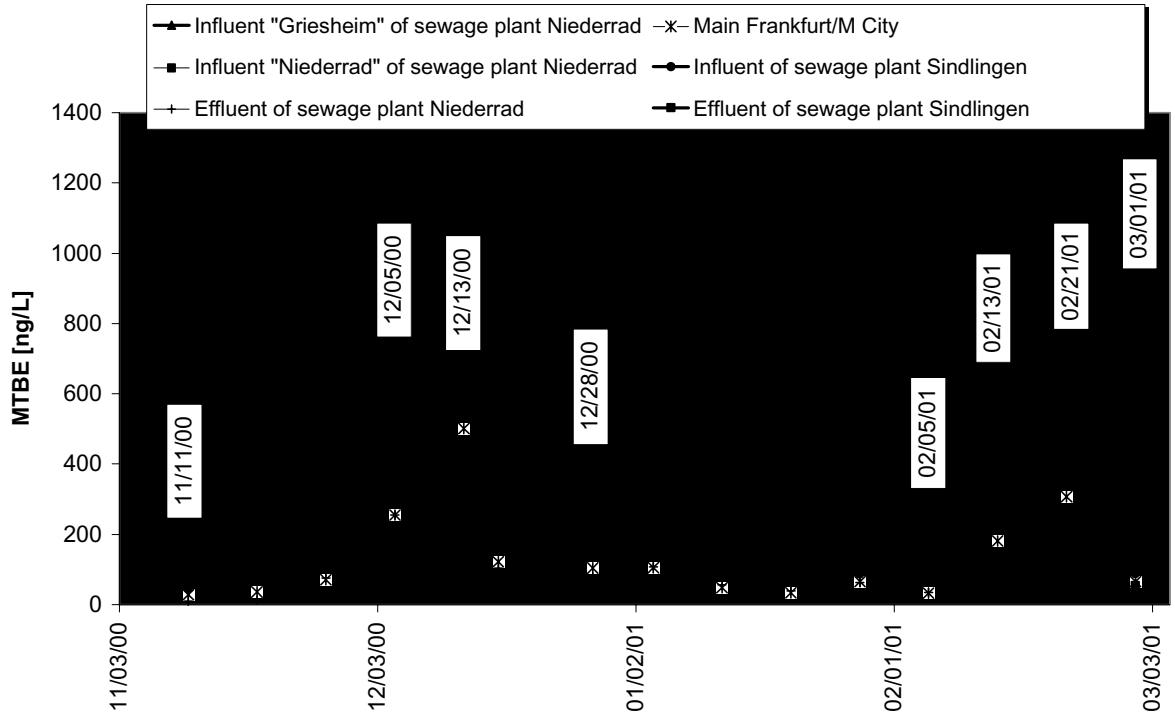


Figure 4-13 Methyl tert-butyl ether (MTBE) concentrations (ng/L) in waste water from the sewage plants Frankfurt/ M-Niederrad, Sindlingen and in Main water at Frankfurt/ M city from 11/11/00 – 03/01/01. Different sampling methods used are described in the text. The detection limit of the method was 10 ng/L with a relative standard deviation of 11 %.

– 12/28/00) to 275 ng/L (272 ng/L, 12/28/00 – 03/01/01). From the limited corresponding data, an elemination rate cannot be calculated. The results of 19 industrial effluent samples of companies in the Frankfurt/ M area show two exceptional high inputs of 12,4 µg/L and 28,4 µg/L, whereas concentrations in other samples were generally low (median of 45 ng/L and mean of 82 ng/L). Detection frequencies for all waste water samples (n = 82) were 38 %, 33 % and 6 %, falling in the concentration ranges of 50 – 200 ng/L, 200 – 1000 ng/L and higher than 1000 ng/L, respectively (Figure 4-11).

4.2.6 Discussion

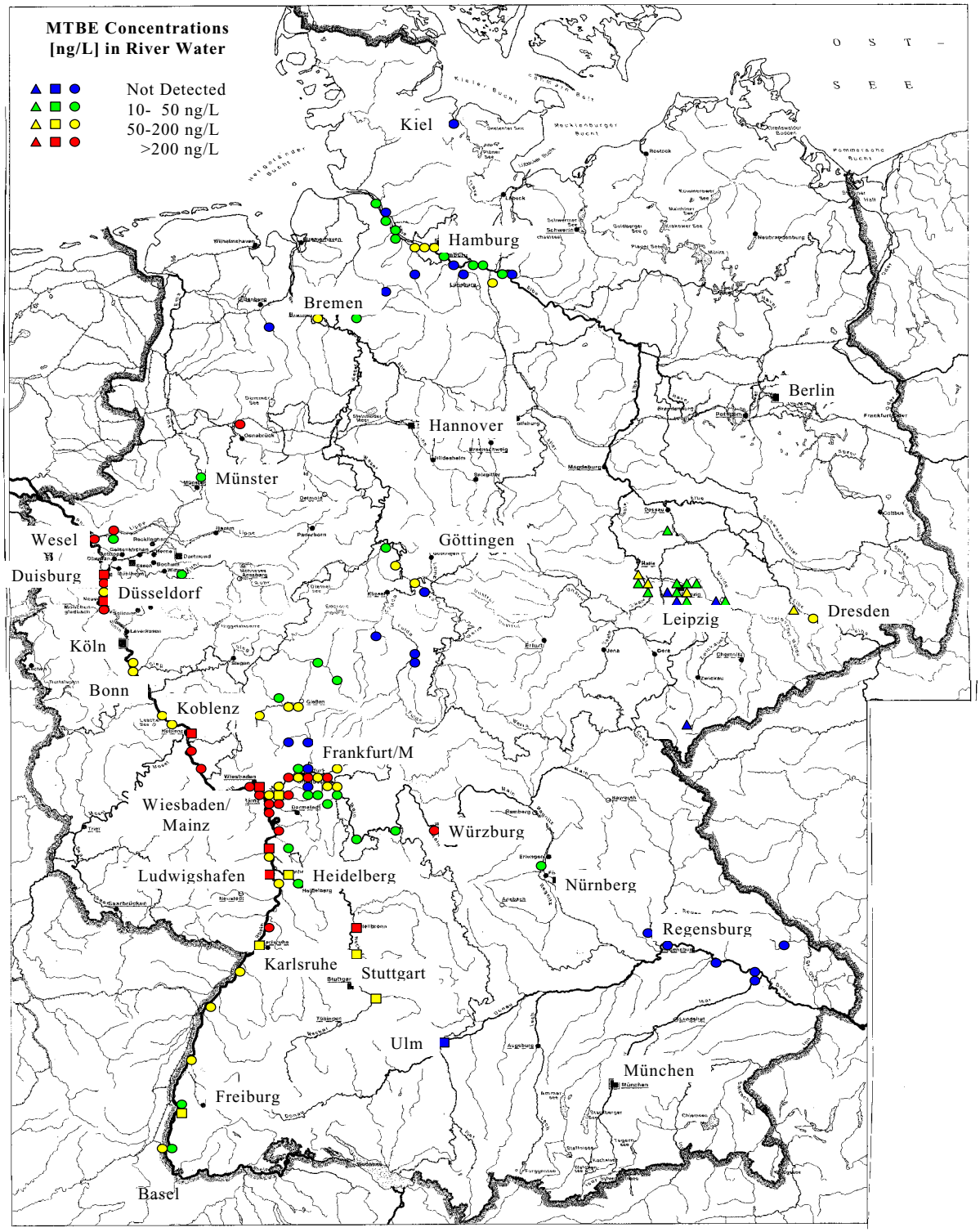
All river water samples of this study and other MTBE data of river water in Germany are summarized in Table 4-3. The sample locations are shown in Figure 4-14.

The observation that higher MTBE concentrations occur in river water near urban agglomerations compared to rural sites was also reported in U.S. studies [REISER AND O'BRIEN, 1998; BROWN ET AL., 2001]. In 1999/ 2000, lower concentrations of 160 ng/L (n = 1) [ACHTEN AND PÜTTMANN, 2000] and 220 ng/L (n = 7) [BRAUCH ET AL., 2000A] were reported for the samples taken at Wiesbaden/ Mainz, compared to the measured concentrations in this study. The resulting MTBE loading in Rhine water at Wiesbaden/ Mainz in 1999 would have been about 3 t/a. In comparison, 1.9 t were released into the Rhine in 1998 by a single company at Ludwigshafen [BASF, 1999]. Mean MTBE concentrations in Rhine water from Mannheim to Duisburg of 233 ng/L and from Vogelgrün to Karlsruhe of 115 ng/L (08/01/99 – 05/01/00) were reported [BRAUCH ET AL., 2000A]. The concentrations are comparable to the results of this study. MTBE concentrations for the upper (Schaffhausen - Karlsruhe) and lower part of Rhine (Karlsruhe - Wesel) are in the range of 70 – 120 ng/L and 230 – 300 ng/L, respectively. Lower concentrations in the upper Rhine from the Bodensee to Karlsruhe/ Mannheim and increasing amounts in the lower part have been found for other Rhine water pollutants and are summarized by the Baseler Modell [SONTHEIMER, 1991]. MTBE concentrations for Main water measured in this study are comparable to the reported mean concentration of 200 ng/L at Bischofsheim (08/01/99 – 05/01/00) [BRAUCH ET AL., 2000A]. MTBE concentrations in water for the upper (Würzburg - Hanau) and lower parts of the Main (Hanau - Bischofsheim) were determined to fall in the range of 20 –50 ng/L and 85 –210 ng/L, respectively. From the Elbe river, low MTBE concentrations were reported for samples taken close to Hamburg (not detected and 13 ng/L) and Dresden (123 ng/L in 1999 [ACHTEN AND PÜTTMANN, 2000] and 141 ng/L in 2000 [EFFENBERGER ET AL., 2001]).

Table 4-3 Summary of methyl tert-butyl ether (MTBE) concentrations (ng/L) in German river water.

River	Location	Sampling Date	Number of samples	MTBE concentration [ng/L]				Reference
				Minimum	Mean	Median	Maximum	
Rhine, upper	Schaffhausen - Rastatt	11/06/00 - 11/07/00	8	13	84	69	195	this study
	Vogelgrün - Karlsruhe	08/01/99 - 05/01/00	8	70	115	-	160	BRAUCH ET AL., 2000
Rhine, lower	Karlsruhe - Wesel	05/11/00 - 01/08/01	52	52	257	254	579	this study
	Mannheim - Duisburg	08/01/99 - 05/01/00	52	100	233	-	990	BRAUCH ET AL., 2000
	Wiesbaden/ Mainz + Nierstein	03/21/99	2	136	148	142	160	ACHTEN AND PÜTTMANN, 200
	Mainz	08/01/99 - 05/01/00	7	120	220	-	400	BRAUCH ET AL., 2000
	Wiesbaden/ Mainz	05/11/00 - 01/08/01	28	107	298	301	579	this study
Main, upper	Seligenstadt	05/29/00 - 01/11/01	4	n.d.	26	23	47	this study
Main, lower	Offenbach - Gustavsburg	05/13/00 - 03/01/01	116	n.d.	186	111	2357	this study
	Frankfurt/ M	01/14/99 + 04/21/99	2	n.d.	12	12	13	ACHTEN AND PÜTTMANN, 200
		05/26/99 - 04/28/00	14	n.d.	42	32	116	this study
		05/13/00 - 03/01/01	24	21	161	114	502	this study
	Bischofsheim	08/01/99 - 05/01/00	36	60	200	-	540	BRAUCH ET AL., 2000
		07/13/00 - 02/21/01	32	27	205	184	547	this study
Elbe	Boitzenburg - Glücksstadt	09/02/00	15	n.d.	40	31	87	this study
	Hamburg	04/22/99 - 02/14/01	9	n.d.	61	59	155	this study
	-	08/01/99 - 05/01/00	2	450	470	465	480	BRAUCH ET AL., 2000
	Dresden	03/28/99	1	-	123	-	-	ACHTEN AND PÜTTMANN, 200
	Rathen, Gaudernitz/ Dresden	03/15/00	2	83	141	141	199	EFFENBERGER ET AL., 2001
Donau	Deggendorf - Regensburg	10/07/00	3	-	n.d.	-	-	this study
	Ulm	08/01/99 - 05/01/00	4	-	n.d.	-	-	BRAUCH ET AL., 2000
Neckar	Mannheim - Deizisau	08/01/99 - 05/01/00	16	50	163	-	1200	BRAUCH ET AL., 2000
	Neckarhausen	09/06/00	1	-	15	-	-	this study
Weser	Bremen + Hemeln	09/02/00 + 09/28/00	2	89	126	126	162	this study
Oder	Frankfurt/ O	03/10/99	1	-	n.d.	-	-	ACHTEN AND PÜTTMANN, 200
Schwarzbach	Trebur near Frankfurt/ M	12/07/00 - 02/21/01	17	38	252	155	1024	this study
Kinzig	Hanau near Frankfurt/ M	12/07/00 - 02/21/01	17	n.d.	94	32	1099	
Nidda	Frankfurt/M - Nied	12/07/00 - 02/21/01	17	n.d.	34	25	87	
Schwarzbach, Kinzig and Nidda	Vicinity of Frankfurt/ M	12/07/00 - 11/29/00	36	n.d.	121	35	1099	
		01/10/01 - 02/21/01	15	33	141	47	1024	
Landgraben	Trebur near Frankfurt/ M	12/07/00 - 02/21/01	4	50	1171	1183	2267	
Lahn	Coelbe - Limburg	12/07/00 - 02/21/01	22	n.d.	82	43	293	
Small creeks	Germany	06/13/00 - 11/29/00	38	n.d.	26	12	198	this study
Channels		06/13/00 - 11/29/00	6	28	83	52	204	

Figure 4-14 Methyl tert-butyl ether (MTBE) concentrations (ng/L) in surface water in Germany. Triangles, Squares and circles indicate results from EFFENBERGER ET AL. [2001], BRAUCH ET AL., [2000A] and this study, respectively.



For two samples (sample location was not noted), significantly higher concentrations of 450 ng/L and 480 ng/L were reported [BRAUCH ET AL., 2000A] in 1999/ 2000. Due to significantly varying MTBE concentrations in the Elbe water and the limited sample set, a characteristic mean value cannot be calculated. Urban creeks with industrial input (Schwarzbach and Landgraben) contain high pollutant concentrations, which is the result of large amounts of household and industrial wastewater emitted into the creeks [HLUG, 1997]. On an annual basis, Schwarzbach water is comprised of an average of 54 % waste water at mean stage and 100 % at low stage. The Nidda creek is also characterized by a high proportion of wastewater but it mainly originates from housing areas and not from industry [POST ET AL., 1999]. The median MTBE concentration of 25 ng/L found in Nidda water is low and indicates that industrial input is the dominant source of the ether in river water at higher concentrations. Fluctuating concentrations in Lahn water and exceptionally high amounts in Lippe water may be the result of industrial inputs. Increased MTBE concentrations in water on 10/23/00 for different small creeks indicate the importance of precipitation events. An increased MTBE concentration was also observed for a precipitation sample collected at Frankfurt/ M city from 10/19/00 - 10/23/00. An amount of 80 ng/L was measured in contrast to common concentrations of up to 30 ng/L the previous months and until the end of October [ACHTEN ET AL., 2001A]. Interestingly, these were the first days of the year with a mean ambient temperature lower than 10 °C. Further, there were only small amounts of precipitation (0.5 mm) on these days. Maximum MTBE concentrations in precipitation may have contributed to higher measurable concentrations in river and creek water.

The results of the river water measurements show a tendency towards increasing MTBE concentrations since 1999 (Figure 4-15). Higher MTBE concentrations in wintertime compared to summertime [REISER AND O'BRIEN, 1998] were not observed. This could be the result of the short-term sampling in this study and low or increasing MTBE concentrations in Germany.

The results of the investigated sewage plant samples show that high MTBE concentrations originate from industrial effluents. Brauch et al. [2000A] measured higher MTBE concentrations in an industrially impacted area at the Rhine, even as much as about 1000 ng/L, which is comparable to the results of this study. Concentrations of the oxygenate of up to 1000 µg/L in industrial effluents were observed [MEF, 2001]. Generally, MTBE concentrations in industrial effluents appear to be low but some exceptionally high concentrations in the µg/L range sometimes occur, which was also observed by BROWN ET AL., [2001] in California Increased concentrations in the effluent of the sewage plant Niederrad (642 ng/L, 12/13/00)

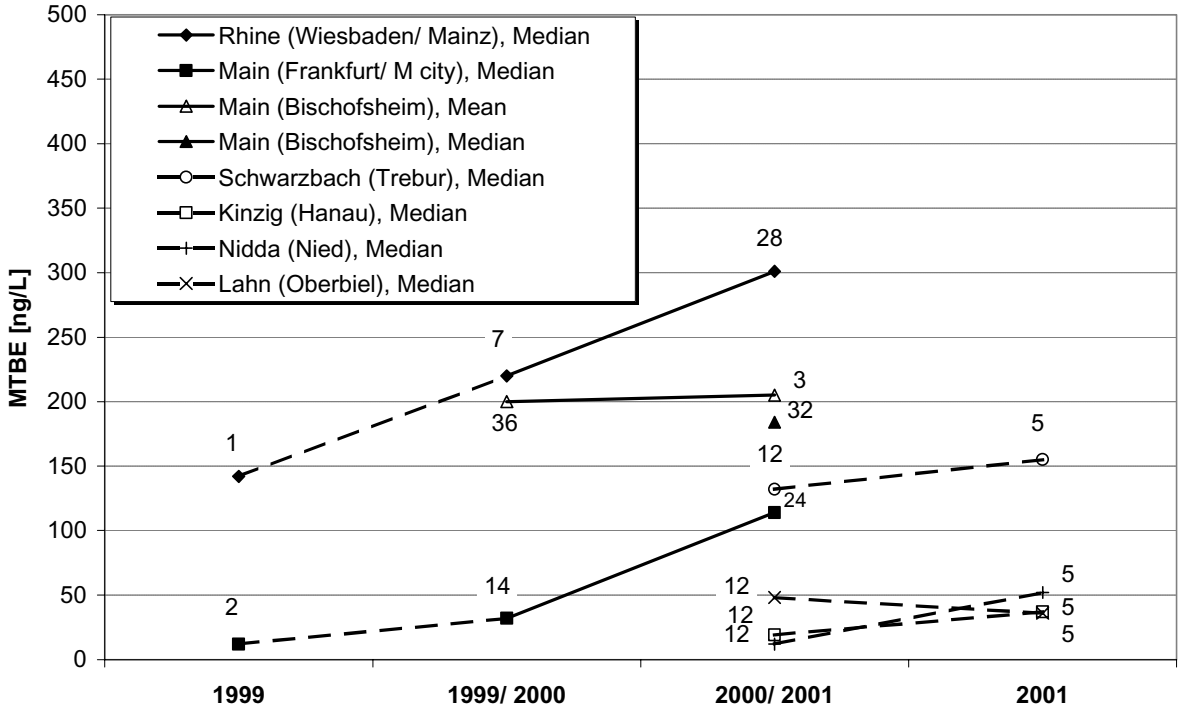


Figure 4-15 Methyl tert-butyl ether (MTBE) concentrations (ng/L) in water from the Rhine and Main rivers and small urban creeks from 1999 – 2001. Numbers indicate sample amounts. Published Rhine water concentrations in 1999/ 2000 [BRAUCH ET AL., 2000A] were used for the calculation of the mean value. The detection limit of the method was 10 ng/L with a relative standard deviation of 11 %.

one week after an increased amount in Main water (502 ng/L, 12/05/00) was measured may be a coincidence because this situation occurred only once. This is supported by the fact that sewage water needs only about 12 h to pass through the plant. Increased MTBE concentrations in water from the plant were observed on 02/21/01, correlating with higher MTBE amounts in precipitation [ACHTEN ET AL., 2001A]. Higher MTBE concentrations at Frankfurt/ M city in precipitation were detected from 02/07/01 – 02/13/01 (74 ng/L) and from 02/13/01 – 02/22/01 (70 ng/L) compared to common concentrations up to 30 ng/L. This increase was restricted to the Frankfurt/ M area. It is not clear if the MTBE increase in domestic waste water from late 2000 to early 2001 were the result of low temperatures in wintertime or of generally increasing concentrations, a trend which could have been overlooked as no samples were analyzed in summertime. Similar MTBE concentrations in the

Main river and effluent water from the sewage plant Niederrad from 11/11/00 to 02/05/01 were observed (at each sampling date both spot samples were collected within a 15 min interval). It can be concluded that a steady state of MTBE input into water versus output by transport and volatilization from river water may be responsible for this observation. Elimination rates of the oxygenate in sewage plants were calculated and percentages of 43.1 %, 56.8 %, 0.1 % and 0 % for amounts evaporated, released (dissolved) into water, adsorbed to sludge and degradated were reported, respectively [MEF, 2001].

The MTBE concentrations in Germany are compared to data from California because the oxygenate has been analyzed frequently in this state and California has a size comparable to Germany (Table 4-4). MTBE concentrations in urban air in the Frankfurt/ M area were measured in 1997 and were roughly in the range from 0.3 – 0.8 ppb_V [RIEDEL, 2001]. A rural atmospheric MTBE concentration of very roughly 0.1 µg/m³ is estimated by use of an average concentration of 20 ng/L of MTBE in German precipitation.
The amounts measured in Germany might be expected to be lower by a factor of appoximately 6 - 7 because the theoretical annual MTBE loading is about 6 times lower compared to California. This is supported by the measured MTBE amounts in small urban creeks without industrial input (factor 4 - 9) and possibly by the MTBE content in urban runoff, if the limited sample amount (n = 12) in Germany is considered. The comparison of MTBE concentrations in river water in California (or New Jersey) and Germany are difficult. Average river water concentrations of 420 ng/L of MTBE in New Jersey [REISER AND O'BRIEN, 1998] and 1400 - 11,530 ng/L in California [Brown et al., 2001] are lower by a factor of 3 - 64 compared to the amounts measured in Germany and Italy (2.9 % of MTBE in gasoline) [PIAZZA ET AL., 2001] of 150 – 200 ng/L. The MTBE concentrations in effluents can also hardly be compared because of the fluctuation of the amounts measured. In urban air, a factor of 3 - 17 is observed between the Californian and German amounts of the oxygenate. It is noteworthy that measured atmospheric MTBE concentrations in the city of Frankfurt/ M are again about one order of a magnitude higher than measured MTBE concentrations in precipitation in the city as decribed earlier [ACHTEN ET AL., 2001A]. Low measured concentrations in precipitation and higher amounts in the air may represent the degradation process in the atmosphere or the photochemical degradation of MTBE in the gas phase and the chemical degradation in the water phase.

Table 4-4 Comparison of methyl tert-butyl ether (MTBE) data in Germany and California.

		Germany	Estimated Factor	California	References Germany	References California
MTBE Use	[mio t]	0.5	7	3.52	PAHLKE ET AL., 2000	HAPPEL ET AL., 1998
Mean concentration in gasoline	[%]	1.2 - 1.7	7 - 9	11	PAHLKE ET AL., 2000; MEF, 2001	HAPPEL ET AL., 1998
Area	[km²]	357 028	1.1	411 012	-	-
Theoretical MTBE load	[t/km²/a]	1.4	6	8.6	-	-
		Environmental MTBE Concentrations (Median/ Mean)				
Small urban creeks without industrial input	[ng/l]	35/ 70	4 - 9	300/ 400	this study	BENDER ET AL., 2000
Urban runoff	[ng/l]	100/ 200	8 - 14	1400 - 1500/ --	this study	DELZER ET AL., 1996; LOPES AND BENDER, 1998; BAY AND BROWN, 2000; BROWN ET AL., 2001
Urban creeks with industrial input	[ng/l]	160/ 1200	-	-	this study	-
Rivers	[ng/l]	150/ 180	3 9 - 64	420/ -- 1400/ 11,530	this study	REISER AND O'BRIEN, 1998 (NJ); BROWN ET AL., 2001
Domestic wastewater	[ng/l]	80/ 250	15 - 48	--/ 3800 (max. 64,000)	this study	BROWN ET AL., 2001
Industrial effluents	[ng/l]	(max. 30,000)	-	(max. 1,878,000)	this study	BROWN ET AL., 2001
Precipitation in wintertime	[ng/l]	not detected - 23/ 14 - 30	1 - 14	90 - 420/ -- (calculated) 25/ 35 (calculated)	ACHTEN ET AL., 2001A	BAEHR ET AL., 1999 and 2001 (NJ), BENDER ET AL., 2000
Urban air	[ppb_V]	--/ 0.03 - 0.8	3 - 17	--/ 0.5 - 2	RIEDEL, 1998	BENDER ET AL., 2000
Rural air	[ppb_V]	--/ 0.03 (estimated)	3 - 17	--/ 0.1 - 0.5	this study	BENDER ET AL., 2000

4.2.7 Conclusions

It can be concluded that varying amounts of MTBE are transported from different sources into river water. Peak concentrations up to about 30 µg/L were measured in industrial waste water effluents. These effluents can be regarded as point-sources and are rapidly diluted in the river water system. This input has not been considered before because only 1.5 % of the produced amount of MTBE in Germany is used for industrial processes. However, this amount should not be neglected because MTBE has unfavorable physico-chemical properties that are responsible for its persistent behavior over long distances in water. Further investigations of direct emission sources into water should be subject of future study. Urban runoff and domestic waste water can be ranked as the second largest source for MTBE in rivers yielding concentrations in the range of 50 – .500 ng/L. The major source of MTBE in urban runoff is thought to originate from vehicle exhaust washed out during precipitation events. The third input of MTBE to river water originates from precipitation enriched by MTBE in amounts of up to 85 ng/L in urban areas in wintertime. MTBE emissions from recreational boating are not the main emission source for the amounts observed in water from the Main and Rhine river. The results from the analysis of river water samples indicate a tendency towards increasing MTBE concentrations since 1999.

From 2005 on, the European and German MTBE use can be expected to have doubled. In 1999, the German MTBE amounts used and measured in small urban creeks without industrial input, urban runoff and urban air might be roughly 6 - 7 times lower compared to California and would still be about 2 - 3 times lower from 2005 on.
An increase in European MTBE consumption of about 63 % can be expected to occur between 1999 and 2010.

4.3 MTBE in Bank-Filtered Water and Drinking Water Produced by Riverbank Filtration

4.3.1 Abstract

Bank filtration of river or lake water represents an efficient and natural purification process used for the drinking water production in many countries and at an amount of about 15 % in Germany. From experiences over decades particularly at the river Rhine and Elbe, it is known that the occurrence of persistent pollutants in river water can represent a problem for the quality of drinking water produced by bank filtration. The common detection of the gasoline additive methyl *tert*-butyl ether (MTBE) in drinking water and the announced phase-out of the oxygenate in the U.S. show that MTBE can contaminate large water amounts due to its phycico-chemical properties. The MTBE situation in the U.S. differs from Europe and significantly lower concentrations in the German environment can be expected. Average MTBE concentrations of 200 –250 ng/L in the Lower Main and Lower Rhine river in 2000/ 2001 were reported.

At two sites at the Lower Rhine and Lower Main rivers MTBE concentrations in bank filtered water (n = 22), recovering well water, raw water and drinking water produced by a water utility at the Lower Rhine site (n = 30) and tap water at Frankfurt/ M city (n = 13) are analyzed from 1999 – 2001. Sample analysis is performed by a combination of headspace-solid-phase microextraction (HS-SPME) and gas chromatography/ mass spectrometry (GC/ MS) with a detection limit of 10 ng/L and a relative standard deviation of 11 %. At the Lower Rhine site, up to 80 m from the river, an average MTBE concentration of 88 ng/L in riverbank filtered water, recovering well water and raw water (n = 7) and of 43 -110 ng/L in drinking water (n = 3) result. At the Lower Main site up to 400 m from the river MTBE concentrations from 52 - 250 ng/L (n = 7) were measured. Tap water samples at Frankfurt/ M (mean of 35 ng/L, maximum of 71 ng/L) were in the same range as MTBE amounts in drinking water at the Lower Rhine site. Measured MTBE amounts eliminated by bank filtration at the Lower Rhine site are comparable to other contaminants. The results of this study show that concentrations measured in river water and drinking water are approximately 2 - 3 orders of magnitude lower than the U.S. drinking water standard of 13 µg/L, represent trace-level concentrations and are not of major concern nowadays. However, the unfavorable combination of the occurrence of non-point MTBE emissions and the persistent behavior of the ether in water even at low concentrations should not be neglected in future discussion. The

reported MTBE concentrations are relevant for precautionary aspects. MTBE concentrations in german river water show a tendency towards increasing concentrations since 1999 and in the future possible higher concentrations could represent a risk for the quality of drinking water that is being produced by water utility using bank filtered river water.

4.3.2 Introduction

In many countries of the world, river water represents an important source of drinking water and simoultaneously, the same rivers are used for sewage disposal. This multifunctional use of rivers can lead to serious concern about the drinking water quality. In favorable hydrogeological formations a low-cost process for significantly improving the quality of surface source waters is provided by bank filtration. Surface water is infiltrated into the bank or bottom sediments of a river or lake and is filtered comparable to a slow sand-filter from shallow wells at tens to hundreds meters distance from the bank by pumping of groundwater. Naturally occuring physico-chemical and biological transformations in the bank filtered water during the underground passage are used as a basic step in the purification process that is necessary to meet drinking water quality.

In Europe, for more than a hundred years [SONTHEIMER, 1991], bank filtration of surface water has been used for the drinking water production at the Rhine river [SONTHEIMER, 1991; HOPMANN ET AL., 1993; SCHUBERT, 2000; JÜLICH AND SCHUBERT, 2000; KUEHN AND MUELLER, 2000], Elbe [JÜLICH AND SCHUBERT, 2000; NEITZEL ET AL., 1998; EPPINGER ET AL., 1999; PAUL ET AL., 2001] and more recently at the Danube [JÜLICH AND SCHUBERT, 2000], Ruhr [JÜLICH AND SCHUBERT, 2000; SCHÖTTLER AND SCHULTE-EBBERT, 1995], Main [STADT FRANKFURT/ M], Iller [JÜLICH AND SCHUBERT, 2000], Maas [HOPMANN ET AL., 1993; JÜLICH AND SCHUBERT, 2000], Ebro [REEMTSMA, 1996], Llobregat [MARTIN-ALONSO ET AL., 1997], Drava, Lake Tegel, Lake Constance, Zürichsee and Ijsselmeer [JÜLICH AND SCHUBERT, 2000]. In the U.S., bank filtered water is used from the Ohio, Santa Ana [JÜLICH AND SCHUBERT, 2000], Great Miami [DEBREWER ET AL., 2000], Lower Susquehanna [DALY AND LINDSEY, 1997], Platte [DORMEDY ET AL., 1999], Killbuck rivers [BREEN ET AL., 1995], also in Egypt from the Nile [DEKOV ET AL., 1997] and in India from the Sabarmati river [GURUNDHADA ET AL., 1999]. About 15 - 16 % of the drinking water used is produced by bank filtration and artificial infiltration in Germany [JÜLICH AND SCHUBERT, 2000; KUEHN AND MUELLER, 2000, BDGW, 1999] and most of this part is produced by water utility at the Rhine and Elbe. The dramatic increase in pollution of river water at the Rhine in the 70‘s

resulted in various studies about the removal of anthropogenic organic and inorganic compounds [FRIMMEL, 1996] like adsorbable organic halogens (AOX), polycyclic aromatic hydrocarbons (PAHs), pesticides, surfactants, aromatic sulfonates, aliphatic and aromatic amines, complexing agents, BTEX, phenols, adsorbable organic sulphur (AOS), pharmaceutical residues, endocrine disrupting chemicals, organic iodine compounds, byproducts of the vitamin C production, particles, bacteria, viruses, parasites, micropollutants, ammonia, heavy metals and others [SCHUBERT, 2000; JÜLICH AND SCHUBERT, 2000; NEITZEL ET AL., 1998; EPPINGER ET AL., 1999; PAUL ET AL., 2001; SCHÖTTLER AND SCHULTE-EBBERT, 1995; DORMEDY ET AL., 1999; SCHWARZENBACH ET AL., 1983; DVWK, 1993; GUDERITZ ET AL., 1993; HABERER AND KNEPPER, 1993; ABKE ET AL., 1995; HÖTZL AND REICHERT, 1996; HEBERER AND STAN, 1997; GRISCHEK ET AL., 1998; LANGE ET AL., 1998; JÜTTNER, 1999; POST ET AL., 1999; BRAUCH ET AL., 2000B]. It has been proven that microorganisms and aquifer sediments from the riverbank naturally purify the infiltrating riverwater of suspended solids, parasites, bacteria, viruses and easily degradable pollutants [SONTHEIMER, 1991; SCHUBERT, 2000]. Additionally, the underground passage acts as a barrier particularly against shock loads resulting from emergency situations as chemical spills or defects in industrial wastewater plants [SONTHEIMER, 1991]. However, some compounds (eg. ethylenedinitrilotetraacetic acid (EDTA), some aromatic sulfonates, the pharmaceutical carbamazepine) are persistent during bank filtration and, hence regularly occur in raw water of the water utility [JÜLICH AND SCHUBERT, 2000; BRAUCH ET AL., 2000B]. Since 1995, the behavior of pollutants during the riverbank passage at the study location „Böckinger Wiesen“ near Heilbronn at the river Neckar has been thoroughly investigated [SCHÖTTLER AND SCHULTE-EBBERT, 1995; HÖTZL AND REICHERT, 1996; JÜTTNER, 1999]. Concentration profiles of some selected compounds at the „Böckinger Wiesen“ site up to 50 m from the river are presented in Figure 4-16. At a distance of 50 m, under suboxic conditions, AOS, the complexing agent EDTA and AOX were less degraded compared to toluene, anionic surfactants, atrazine and fragrance compounds. Generally, sufficient degradability of the latter compounds (atrazine is well degradable under anoxic conditions only) and rather persistent behavior of the former group is also frequently noted in literature [DVWK, 1993; RIPPEN, 2000]. Different waterworks at the Rhine river investigated the elimination of persistent and common pollutants like EDTA, AOX and AOS in raw water of the water utility compared to corresponding river water concentrations [SONTHEIMER, 1991; BRAUCH ET AL., 2000B]. During the last decades, water quality has been improved by the reduction of the amount of

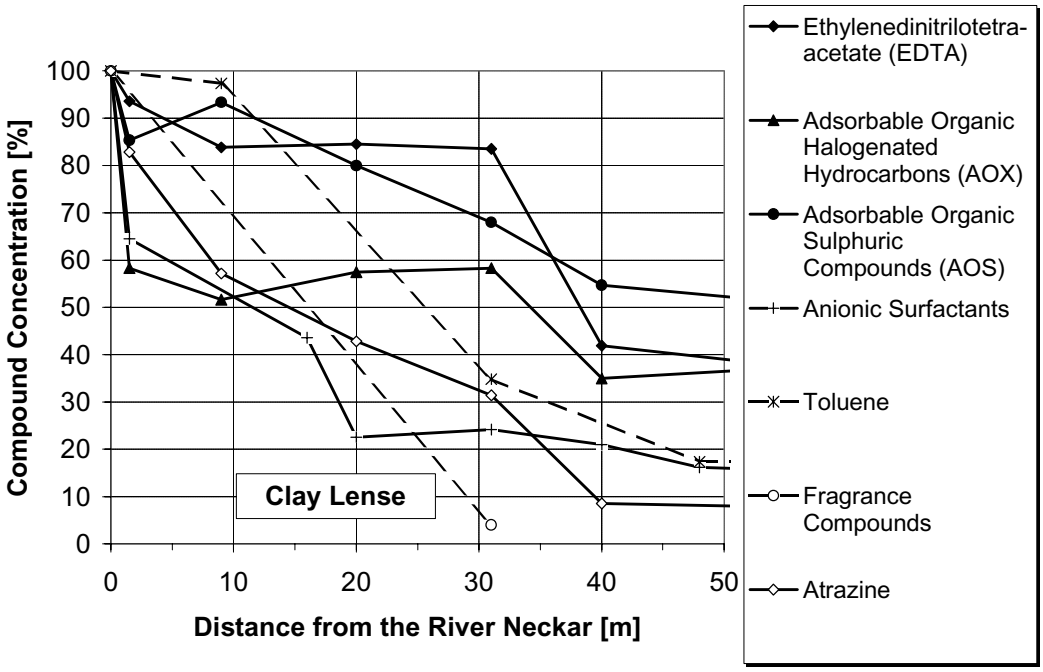


Figure 4-16 Pollutant concentrations (%) in Neckar river water and during the riverbank passage of 50 m from the river at the "Böckinger Wiesen" site near Heilbronn [HÖTZL AND REICHERT, 1996].

chemicals released into river water [KUEHN AND MUELLER, 2000; BRAUCH ET AL., 1999], and by substitution of toxic and persistent by less toxic and biodegradable substances. Improving the technology in sewage purification plants and incineration have also contributed to improved river water quality. A significant increase in the water quality of the river Elbe was a consequence of reduced influx of industrial effluents into the river, following german reunification [JÜLICH AND SCHUBERT, 2000].

Eventhough decreasing concentrations of many pollutants in river water have been recorded, the recent occurrence of the oxygenate methyl *tert*-butyl ether (MTBE) in aquatic environments [REISER AND O'BRIEN, 1998; ZOGORSKI ET AL., 1998; ACHTEN AND PÜTTMANN, 2000; EFFENBERGER ET AL., 2001; BRAUCH ET AL., 2000B] has caused concern in the U.S. and in Germany about the possible national extent of contamination [CLAWGES ET AL., 2001; PAHLKE ET AL., 2000]. Since 1985, MTBE has been added to german gasoline as an octane enhancer and to reduce emissions. With increasing frequency of detection the occurrence of MTBE is observed in the atmospheric and aquatic environment not only on the American continent [REISER AND O'BRIEN, 1998; ZOGORSKI ET AL., 1998; GAFFNEY ET AL., 1999;

CLAWGES ET AL., 2001; BENDER ET AL., 2000] but also in Europe [ACHTEN AND PÜTTMANN, 2000 AND 2001B; ACHTEN ET AL., 2001A AND 2002B; EFFENBERGER ET AL., 2001; BRAUCH ET AL., 2000B; PAHLKE ET AL., 2000; VAINIOTALO ET AL., 1998; SCHIEDEK ET AL., 2000; ZAMBELLAS ET AL., 2000; POULOPOULOS AND PHILIPPOLOULOS, 2000; MRASEK, 2000; PIAZZA ET AL., 2001]. In 1999, the U.S. EPA adopted a drinking water standard of 13 µg/L for MTBE [PIAZZA ET AL., 2001]. Undoubtedly, most amounts of MTBE from oxygenated gasoline reach water by leakage from underground storage tanks (LUSTs) into groundwater. However, another possible pathway for the occurrence of lower MTBE concentrations in drinking water is represented by non-point MTBE input into river water used for the drinking water production by riverbank filtration. The fuel additive in river water is detected in the range of ng/L - µg/L [REISER AND O'BRIEN, 1998; ZOGORSKI ET AL., 1998; ACHTEN AND PÜTTMANN, 2000; ACHTEN ET AL. 2002B; BRAUCH ET AL., 2000A; PIAZZA ET AL., 2001]. In Germany average MTBE concentrations of about 250 ng/L in Rhine water and about 200 ng/L in Main water in 1999/ 2001 [BRAUCH ET AL., 2000A; ACHTEN ET AL., 2002B] might lead to detectable concentrations of MTBE in water from streambed wells. The oxygenate occurred in river water mostly in agglomerated areas due to urban runoff, MTBE containing precipitation (in wintertime only) and industrial effluents [ACHTEN ET AL., 2002b]. It is notable that non-point source emissions (e.g. vehicle emissions) are not limited to specific sites and hence cannot easily be remediated within a short time. Additionally, river water quality in Germany has significantly increased due to legislation that focuses on „reduction at the source principle" and „polluter pays principle" [JÜLICH AND SCHUBERT, 2000]. The former principle fails for diffuse source contaminants as it has been demonstrated for nutrients and pesticides, therefore the „precautionary principle" is of outstanding importance for the drinking water supply with respect to dangerous substances which may come from diffuse sources [JÜLICH AND SCHUBERT, 2000].

In groundwater from the Lower Susquehanna River Basin, MTBE was detected in 16 from 118 well water samples at a concentration range of 110 – 510 ng/L [DALY AND LINDSEY, 1997] and in the Connecticut, Housatonic and Thames River Basins a maximum concentration of 5.8 µg/L MTBE in water from urban streambed wells was reported [GRADY, 1998]. Unfortunately, it is not clear if LUSTs were at least partially responsible for the described detected amounts of the ether. In Germany, MTBE was detected in 5 raw water samples produced from bank filtration at the Lower Rhine in the range of 50 – 100 ng/L in 1999/ 2000 [BRAUCH ET AL., 2000A]. Recently, MTBE has been detected in tap water (80 – 400 ng/L) from different ground water sources in Italy [PIAZZA ET AL., 2001].

In the future, the recalcitrance of the widely used additive in river water could represent a problem for waterworks that produce drinking water from riverbank filtration if river water concentrations will increase. The aim of this study was to investigate the relevance of this pathway at two study sites. To our knowledge this is the first study that investigates the behavior of MTBE during the riverbank passage and the impact on treated drinking water produced by bank filtration.

4.3.2.1 Site Locations

4.3.2.1.1 Water Utility 1 at the Lower Rhine River

The drinking water supply for many cities in the Lower Rhine embayment/ Germany is provided by waterworks situated at the river Rhine. At the investigated site a gallery of recovering wells is situated at a distance of about 50 m, parallel to the Rhine for the drinking water production. The aquifer consists of pleistocenic gravel and sand of the Rhine lower and middle terraces that show a thickness of about 20 m. It is characterized by a field velocity of 5 – 10 m/d**,** a coefficient of permeability of about $1.6 * 10^{-3}$ m/s and a porosity of 20 %. Three multilevel groundwater wells, at distances of about 20 m (well A), 40 m (well B) and 80 m (well C) from the Rhine bank, have been used for several bank filtration quality investigations (Figure 4-17). The same wells (A, B and C at three different depths) were sampled in this study to compare data obtained with existing data. Generally, the water in wells A and B originates from bank filtration. In well C, mostly groundwater inflow from land is found although at high Rhine water levels bank filtration water infiltrates also into well C, leading to a mixture of the two different water types. Due to a colmated and plastered bottom of the Rhine near the bank, river water infiltration mainly occurs at a distance of about 80 – 250 m from the bank by filtration into the river bottom. A residence time of about 15 – 70 d is needed by water infiltrating from the Rhine bottom to reach the monitoring and recovering wells. At the water utility about 75 % of bank filtration water is mixed with approximately 25 % groundwater from natural groundwater recharge. The hydrochemical situation of the aquifer is aerobic and characterized by oxygen reducing conditions. Significant biological acitvity is observed in the bank sediments and it has been proven that transformation of pollutants by microorganisms is most effective in the first decimeters of the river sediment [NEITZEL ET AL., 1998]. Contamination of the investigated bank filtered water by LUST's could be excluded.

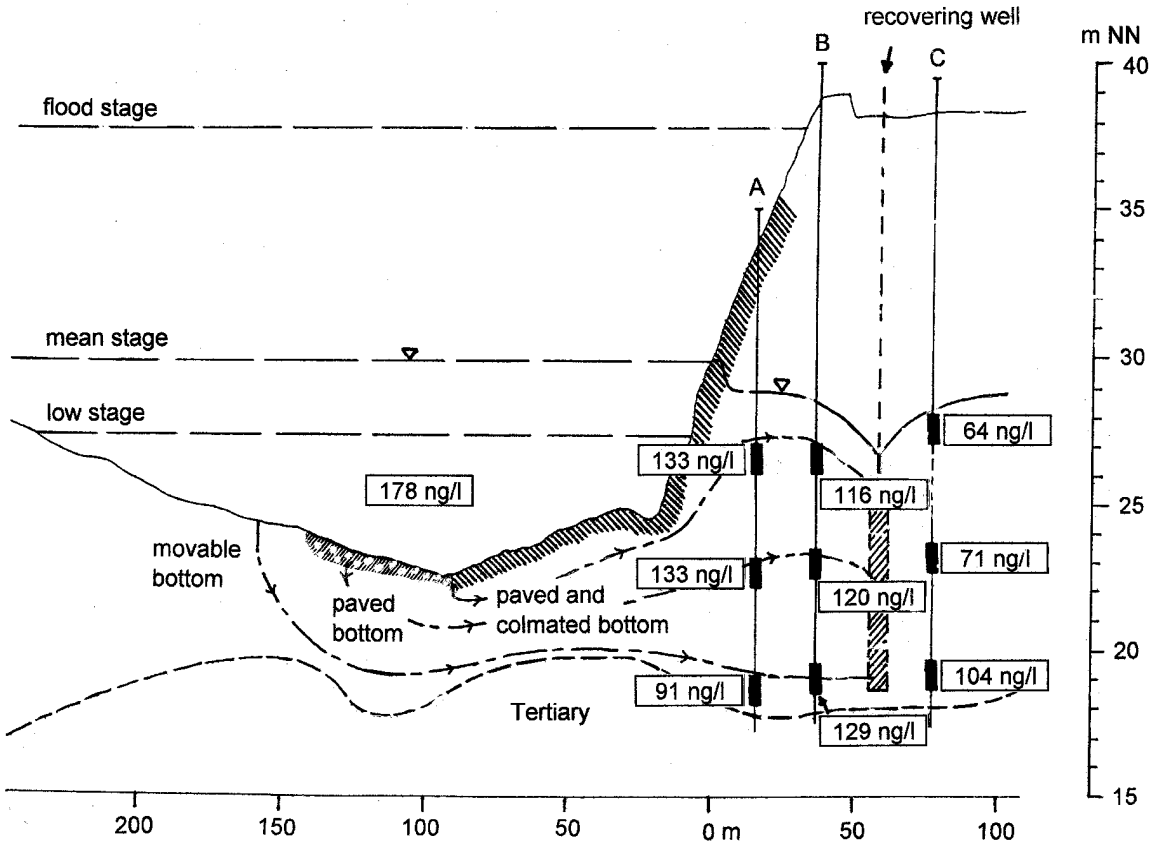


Figure 4-17 Hydrogeological cross section through the Rhine river and bank at the Lower Rhine site (water utility 1). Bank filtration water pathways and flow direction are indicated by dotted lines with arrows. Methyl tert-butyl ether (MTBE) concentrations (ng/L) in water of three monitoring wells up to about 80 m from the bank at three different depths (black) are shown. Samples were collected on 02/13/01. The MTBE concentration of Rhine water at the site represents a mean value (n = 3). The location of a recovering well near the monitoring wells is shown (ruled).

4.3.2.1.2 Drinking Water Purification Processing at Water Utility 1

Pumped water from the recovering wells is treated at the water utility (Figure 4-18) in order to meet drinking water quality requirements. In the first step, raw water provided by the wells is treated by ozone which evokes flocking of mainly ferrous and manganese compounds, while also improving odor and taste of the water. It then remains in an intermediate tank for a period of 40 min for chemical transformations to occur. The carbonic acid concentration is reduced by aeration in the tank to a soluted calcite concentration less than 5 mg/L. In a third step, the water is pumped through two different layers of carbon filters. In the first layer, the water is filtered and most residual contaminants are biodegraded. In a second layer, organic halogenated hydrocarbons and other compounds are adsorbed by porous activated carbon filters. Finally, phosphate, silicate (1 mg/L) and chloride dioxide (0.06 mg/L) are added to the water to prevent corrosion of pipes and biological contamination. During the entire water purification process the temperature of the water remains roughly constant at 13 - 14 °C.

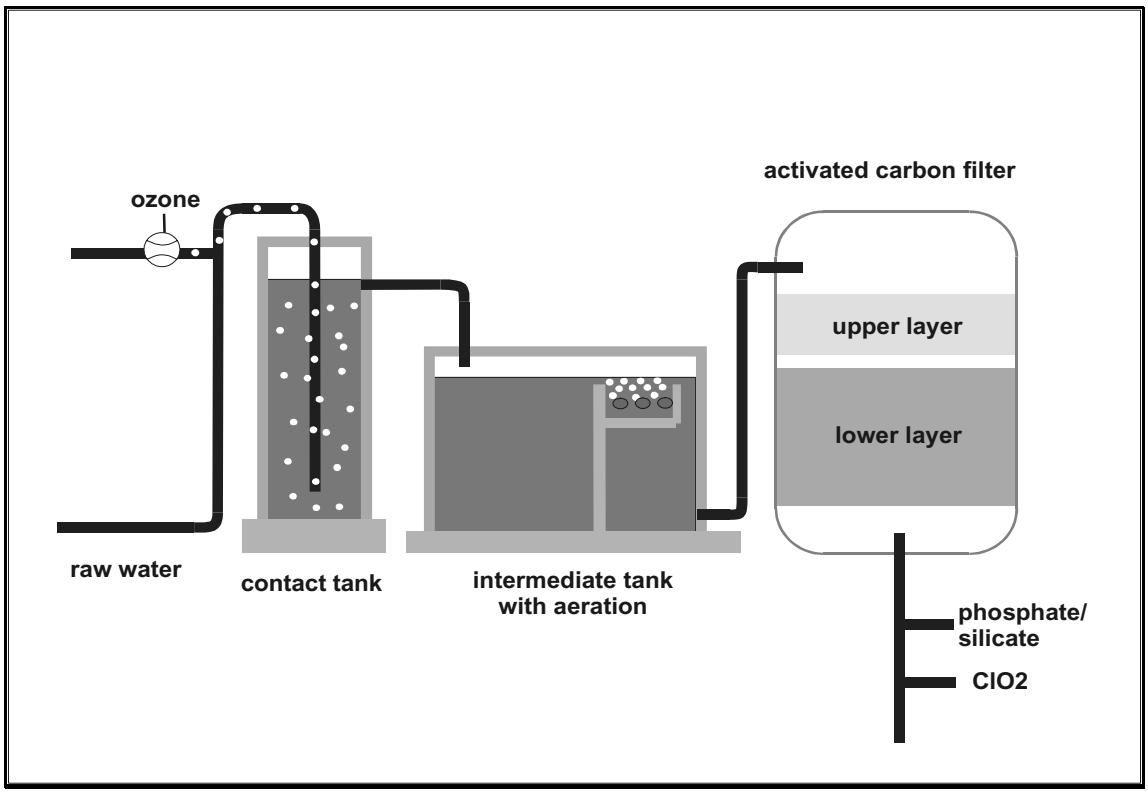


Figure 4-18 Drinking water purification processing at water utility 1.

4.3.2.1.2 Eddersheim at the Lower Main River in the Vicinity of Frankfurt/ M

Bank filtration water of the river Main is used for the drinking water production at several sites in the vicinity of Frankfurt/ M. The study location at Eddersheim has been used for several water quality investigations [ABKE ET AL., 1995; POST ET AL., 1999]. Water from four monitoring wells at distances of 60 m (well 1123), 400 m (well 1184), 1050 m (well 1128) and 1150 m (well 1132) from the Main was investigated in this study. The gallery of recovering wells for the nearby water utility Hattersheim is mostly situated approximately 1300 m parallel to the Main, with a few recovering wells situated as close as about 200 m from the Main. Groundwater in wells 1123 and 1184, situated near the Main, mostly originates from bank filtration, although to a small amount inflow of groundwater from the land occurs at 400 m [POST ET AL., 1999]. It is noted that all four investigated wells are not situated in a line within the same flow direction near the river as is the case at the Lower Rhine site. Nowadays, groundwater in wells at distances of more than 1000 m from the Main originates from land only. In the past however, water from bank filtration was transported into the aquifer from the river towards the water utility Hattersheim due to significantly higher pumpages. The aquifer consists of about 10 – 15 m pleistocenic and about 65 – 70 m pliocenic gravel and sand (containing some confined clay lenses), with characteristic coefficients of permeability of about $2 * 10^{-4} – 2*10^{-3}$ m/s and $3 – 5*10^{-4}$ m/s, respectively. Groundwater between the Main and the well 1184 at 400 m distance is characterized by a field velocitiy of 0.7 – 1.3 m/d with resulting residence times of 45 – 85 d for well 1123 and 310 – 570 d for well 1184. The hydrochemical situation in the aquifer, up to well 1184, is characterized by iron (up to 3.6 mg/L) and manganese (up to 5.2 mg/L) reduction. Median Main water concentrations from 1995 - 1999 show that the oxygen (11 mg/L) and nitrate concentrations (23 mg/L) in the Main water are reduced during the passage from the Main to well 1123 (1.3 mg/L oxygen and <0.5 mg/L nitrate at –90 mV redox potential) and do not change significantly until well 1184 (2.4 mg/L oxygen and <0.5 mg/L nitrate at –25 mV redox potential). Therefore, biological activity under oxygen, nitrate, iron and manganese reducing conditions during the riverbank passage can be expected. At a distance of more than 1000 m from the riverbank, oxygen concentrations (about 10 mg/L) and nitrate concentrations (about 60 mg/L), fall within the normal range for agriculturally used land. Contamination of the investigated bank filtered water by LUST's or leakage from sewage pipes cannot be excluded because the wells are situated in a housing and industrialized area.

4.3.3 Sampling

Collection of all samples was performed by single point sampling. Three Lower Rhine water samples near the site were collected on the 02/06/01, 02/08/01, 02/10/01, with the mean value of the measured MTBE concentrations subsequently calculated. Samples at the monitoring wells A, B and C, at three different depths, were taken on 02/13/01. Water from the recovering wells, raw water and drinking water at three waterworks were collected on 02/07/01, 02/08/01 and 02/12/01, respectively. The results obtained did not correspond to the monitoring well samples data. Additionally, samples from a water storage tower (02/08/01) and other groundwater from a cross link (02/07/01) were taken. Samples from the four monitoring wells at Eddersheim were collected on 11/18/99, 04/06/00, 01/31/01 and 05/09/01. Potable water samples (n = 13) were collected from taps (after 15 minutes of water flow) at the University of Frankfurt/ M, situated in the centre, from 11/16/00 - 03/01/01.
Water samples were stored in 100 mL sample vials (brown glass), acidified beforehand by concentrated (33%) hydrochloric acid. The bottles were completely filled with no headspace left, cooled to 4 °C and analysed within 3 weeks after sampling.

4.3.4 Results

4.3.4.1 MTBE in Bank Filtration Water and in Water from Water Utility 1 at the Lower Rhine River

Rhine water samples showed MTBE concentrations of 310 ng/L, 125 ng/L and 99 ng/L on 02/06/01, 02/08/01 and 02/10/01, respectively, with a mean concentration of 178 ng/L resulting. After a distance of about 20 m (well A) from the riverbank, the MTBE concentration was reduced by about 35 % compared to the mean Rhine water concentration. (Figure 4-17). The deepest monitoring well only receives water infiltrating through the movable and paved bottom of the Rhine with the residence time about twice as high as compared to the upper and middle wells. This results in a measurable reduced MTBE concentration of about 50 % compared to the mean Rhine water concentration and represents 25 % less than the concentrations in the middle and upper wells. At a distance of about 80 m (well C) from the Rhine riverbank, MTBE is detected at concentrations of about 60 –100 ng/L (about 35 – 55 % of the mean Rhine water concentration) which represents a diluted concentration by groundwater from the land (MTBE was not analyzed in groundwater from the land only). Lower concentrations occur in the upper wells. The conditions in the aquifer

during the sampling were period oxic (5 - 9 mg/L oxygen, except lowest monitoring well C with 0.3 mg/L).

About a week before, sampled water at the water utility 1 from two recovering wells and raw water showed MTBE concentrations in the range of 100 – 120 ng/L (Figure 4-19). The mean concentration of 101 ng/L in the monitoring wells near a recovering well (middle and deep monitoring wells B and C) a week later was in a comparable range. In recovering well water and raw water at two waterworks close to waterworks 1 (2 and 3), the MTBE contents were slightly lower with values of 60 – 90 ng/L. Also a lower MTBE concentration of 43 ng/L was detected in drinking water at water utility 1 due to the purification processing. At water utility 2 the concentrations of 62 ng/L and 110 ng/L were in the range of recovering well and raw water data. The persistent behavior of MTBE is further documented by measurable concentrations in water of a watertower (42 ng/L). MTBE was not detected in the sample of other groundwater transported to the water utility 1 by a cross link.

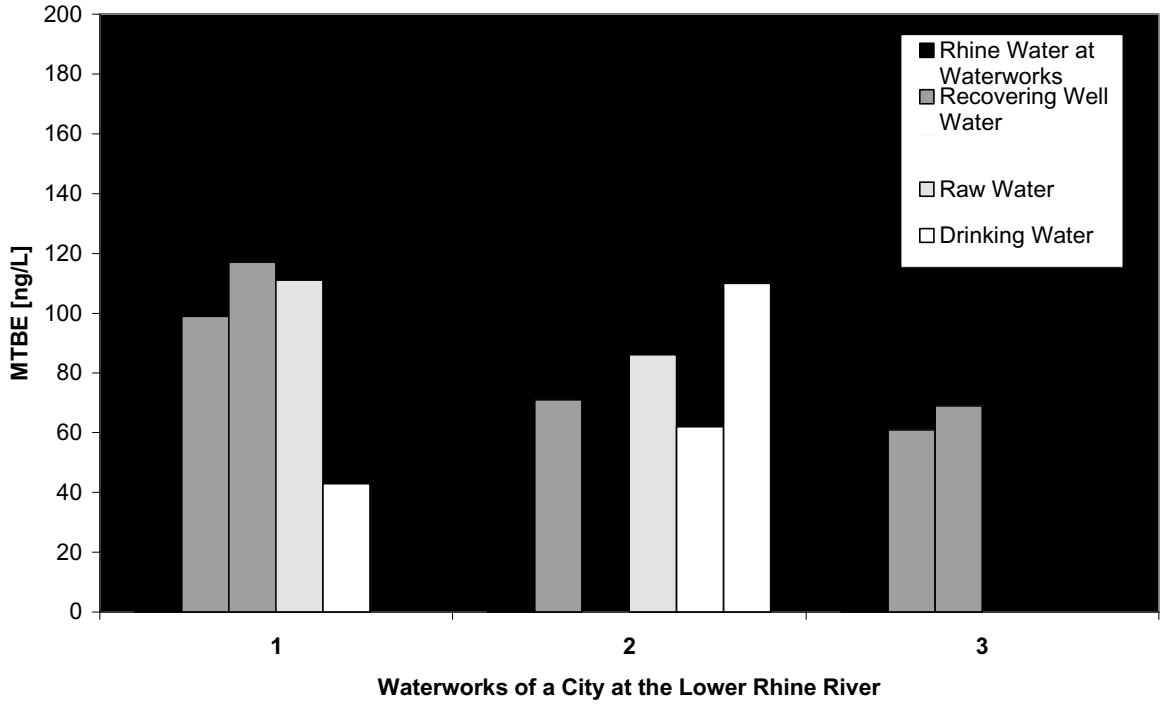


Figure 4-19 Methyl tert-butyl ether (MTBE) concentrations (ng/L) in recovering well water, raw water, drinking water and Rhine water (mean) at three waterworks belonging to water utility 1 in the Lower Rhine embayment.

4.3.4.2 MTBE in Bank Filtration Water at the Main River

Median and mean Main water concentrations for the three bank filtration sampling dates on 11/18/99, 04/06/00 and 01/31/01 were calculated from analyzed Main water samples at Frankfurt/ M [ACHTEN ET AL., 2002B]. Due to the small sample amount (n = 15) and the constantly low concentrations (maximum of 116 ng/L) in the period from 01/14/99 - 04/06/00 the median (mean) MTBE concentration of 29 ng/L (39 ng/L) in Main water was used for comparison to both bank filtration samplings on 11/18/99 and 04/06/00. For the third bank filtration sampling on 01/31/01, measured MTBE concentrations in Main water during 10/24/00 – 01/28/01 were used and a median (mean) MTBE concentration of 71 ng/L (100 ng/L) was calculated. For the sampling on 05/09/01 a median (mean) concentration of 211 ng/L (580 ng/L) in the time from 02/05/01 - 05/09/01 resulted according to the residence times needed for river water being transported to well 1123 and 1184. The results of the different samplings are shown in Figure 4-20. At the sampling dates in the years 1999 - 2000 low MTBE concentrations of about 50 ng/L are observed in Main water and in the well

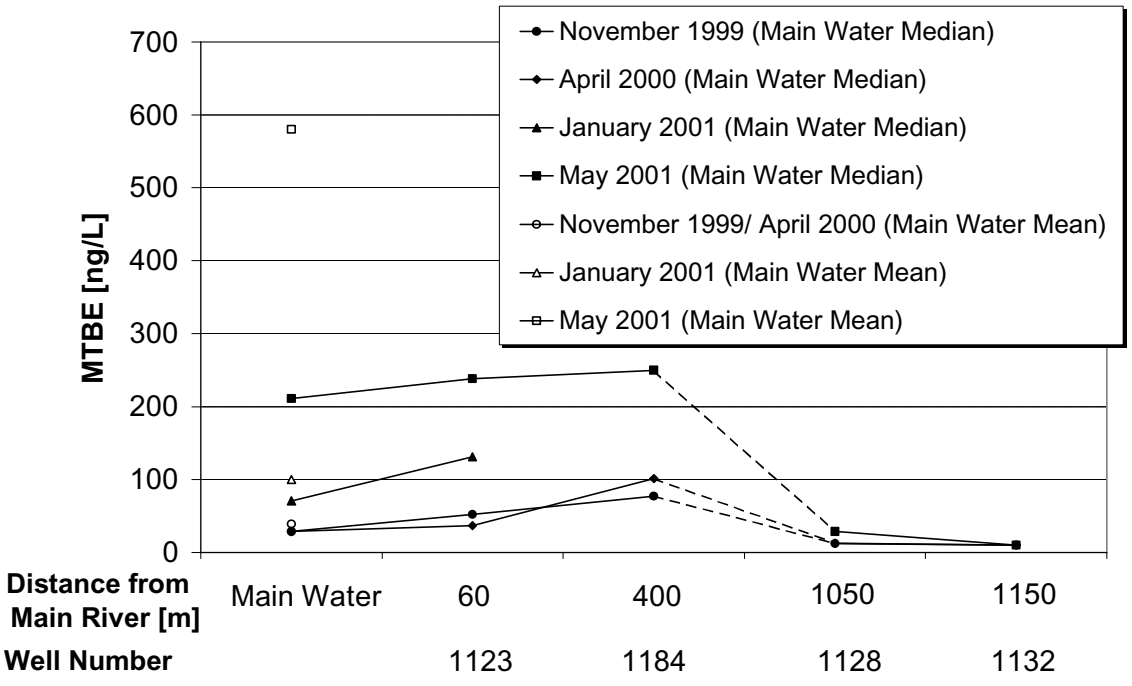


Figure 4-20 Methyl tert-butyl ether (MTBE) concentrations (ng/L) in Main water (mean/ median) and during bank filtration at the Hattersheim site in the vicinity of Frankfurt/ M from 1999 to 2001.

1123 at a distance of 60 m from the Main. In January 2001, the MTBE concentration slightly increased in Main water (71 ng/L) and in the well 1184 at 60 m distance (131 ng/L). At all sampling dates the MTBE concentrations in water from well 1184 did not vary significantly from the data of well 1123 except that they generally are even slightly higher and not lower as it would be expected with increasing distance from the river due to attenuation processes. In May 2001, MTBE concentrations in Mainwater (02/05/01 – 05/09/01) increased to a median (mean) concentration of 211 ng/L (580 ng/L) and also concentrations in bank filtration water were higher (238 ng/L in 1123, 250 ng/L in 1184). In groundwater from the landside at a distance of 1050 m from the Main only traces of MTBE were detectable and at a distance of 1150 m from the river, MTBE was below the detection limit of 10 ng/L in the well water at all samples.

In the winter months of 2000/ 2001 MTBE was also present in drinking water samples (n = 13) from the tap at the Intitut für Mineralogie –Umweltanalytik of the University Frankfurt/ M with a median (mean) concentration of 32 ng/L (35 ng/L) and a maximum of 71 ng/L.

4.3.5 Discussion

All analyzed MTBE concentrations were far below the EPA drinking water standard of 13 µg/L and represented trace level concentrations. The calculated mean MTBE concentration of 178 ng/L in Rhine water at the sites of the water utility 1 is slightly lower but in the range of reported data of 210 ng/L [BRAUCH ET AL., 2000A], 234 ng/L and 216 ng/L [ACHTEN ET AL., 2002B] in 1999 – 2001. This is confirmed by observed mean values in Rhine water between Mainz and Duisburg of 255 ng/L (n = 50) [ACHTEN ET AL., 2002B] and 235 ng/L (n = 29) [BRAUCH ET AL., 2000A] in 1999 – 2001. MTBE concentrations, obtained from water in the monitoring wells and raw water show that the reported MTBE data in the monitoring wells represent the MTBE situation at the water utility 1 during the sampling periods. MTBE of roughly 200 ng/L in the river water was reduced during the riverbank passage to roughly 100 ng/L and was not eliminated to a greater extent. This observation is supported by MTBE concentrations in the range of 70 - 110 ng/L obtained at water utility 2 and 3 during the same period.

The data allow to conclude that the behavior of MTBE, during the riverbank passage at the described Lower Rhine site, is even at approximately 100 - 400 times lower comparable to river water concentrations of other persistent compounds present in the Rhine water like

EDTA [JÜLICH AND SCHUBERT, 2000], adsorbable organic halogenated hydrocarbons (AOX) or AOS (Figure 4-21). It is important to note that the AOX concentrations have decreased significantly since 1988 [JÜLICH AND SCHUBERT, 2000]. In this study however, the AOX

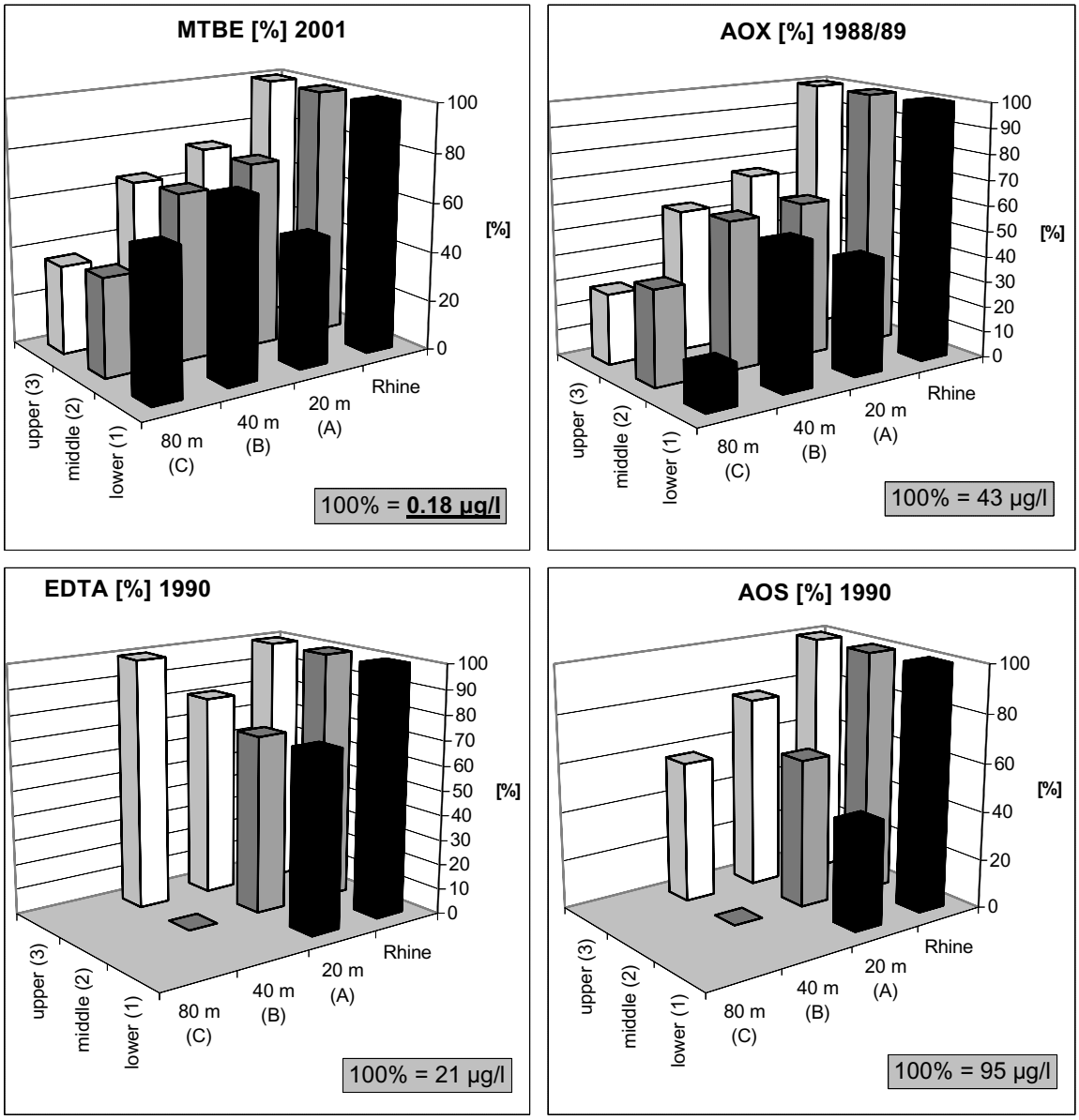


Figure 4-21 Methyl tert-butyl ether (MTBE) concentrations (µg/L) during the riverbank passage at water utility 1 in the Lower Rhine embayment in relative comparison (%) to concentrations of adsorbable organic halogenated hydrocarbons (AOX), ethylenedinitrilotetraacetic acid (EDTA) and adsorbable organic sulphur (AOS) [SONTHEIMER, 1991]. Note that MTBE concentrations in Rhine water are at least two orders of a magnitude lower than other pollutant concentrations.

concentration profiles measured in 1988 are only used to compare the behavior of the different compounds. In future discussion of data from the water utility 1 at the Lower Rhine only wells situated closest to the riverbank (up to 20 m) are considered, as microbial activity is highest in the first centimeters of the bank and with increasing distance from the river the influence of other diluting groundwater also increases. During the first 20 m of bank filtration at water utility 1 EDTA, AOX, AOS and MTBE were eliminated by approximately 20 – 30 %, 35 – 55 %, 20 – 55 % [SONTHEIMER, 1991] and 25 – 50 %, respectively, due to natural attenuation processes under aerobic conditions. Lower concentrations in the lowest well A were often observed, presumably resulting from degradation and adsorption processes, as the residence time was higher than that of the upper and middle wells, volatilization processes can be excluded and a 100 % origin of river filtration water a few meters below the river bottom can be assumed. As MTBE is poorly adsorbed, the degradation of the ether under oxygen reducing conditions [BRADLEY ET AL., 2001A], is likely. During several sampling times, EDTA, which has been widely reported as being poorly degradable [JÜLICH AND SCHUBERT, 2000; RIPPEN, 2000], was persistent even in the lowest well A [SONTHEIMER, 1991], whereas AOX and AOS were present in lower concentrations which is indicative of some degradation/ adsorption abilities that were reported in previous studies [GRISCHEK ET AL., 1998; BRAUCH ET AL., 2000B]. During further transport through the underground network at water utility 1, low MTBE elimination is observed, occuring mainly in the upper wells, probably due to volatilization or dilution by other groundwater. Eighty metres from the bank, 104 ng/L of MTBE were still detectable in the deepest monitoring well C (Figure 4-17) and it remains unclear if it originates from riverwater or from groundwater from the land.

Much effort has been spent to understand the behavior of pollutants during the riverbank passage up to hundreds of meters from the river [SONTHEIMER, 1991; SCHÖTTLER AND SCHULTE-EBBERT, 1995; DVWK, 1993; HÖTZL AND REICHERT, 1996]. Extensive investigations at different locations revealed that simple dilution with other groundwater that does not originate from bank filtration and different hydrogeological/ hydrochemical settings (eg. aquifer material, field velocity, residence times, chemical conditions) were the most important factors which made comparison of different study locations difficult. Different studies conducted at the Rhine (Wittlaer, Cologne and Mündelheim) and the Neckar („Böckinger Wiesen“/ Heilbronn) which investigated the behavior of organic pollutants during bank filtration with similar hydrogeological settings to the situation at water utility 1 were chosen for comparison and are summarized in Table 4-5. For comparison also only the

Table 4-5 Hydrogeological and hydrogeochemical data of the groundwater at waterworks 1 and comparable study locations at Duisburg-Mündelheim, Düsseldorf-Wittlaer, Cologne-Rheinkassel and at the study location "Böckinger Wiesen"/ Heilbronn.

River	Location	Geology	Coefficient of permeability [m/s]	Field velocity [m/d]	Distance of recovering wells from the bank [m]	Residence Time [d]	Amount of bankfiltration water in raw water [%]	Oxygen [mg/L]	Conditions	Reference
Lower Rhine	Waterworks 1	20 m Lower and Middle Rhine terrace	1.6×10^{-3}	5 - 10	60	15 - 70	75 (60 - 80)	< 9	oxic, O_2 and NO_3 reduction, no Fe and Mn reduction	this study
Lower Rhine	Waterworks Duisburg-Mündelheim	7 m Lower and Middle Rhine terrace	1×10^{-3} - 5×10^{-2}	-	30	-	50	-	oxic?	SONTHEIMER, 1991
Lower Rhine	Waterworks Düsseldorf-Wittlaer	15 m Lower and Middle Rhine terrace	2×10^{-3} - 1×10^{-2}	2 - 10	170	15 - 90	60 (50 - 60)	4 - 10	oxic, O_2 and NO_3 reduction, no Fe and Mn reduction	SONTHEIMER, 1991; BRAUCH ET AL., 2000; DENEKE, 1997
Lower Rhine	Waterworks Cologne-Rheinkassel	20 - 25 m Lower Rhine terrace	-	-	160	-	50 (30 - 50) (30 % young, 20 % old)	-	oxic?	SONTHEIMER, 1991
Neckar	Böckinger Wiesen/ Heilbronn	3 - 5 m Valley gravel, at 10 - 30 m from the bank: clay lense	8×10^{-3} - 1×10^{-2}	2 - 3	study distance: 150	40 - 80	0 - 40 m: 80 40 - 150 m: 30 - 80	< 3	0 - 70 m: suboxic, Fe- and Mn reduction, 70 - 150 m: oxic, O_2 and NO_3 Reduction	SCHÖTTLER AND SCHULTE-EBBERT, 1995; HÖTZL AND REICHERT, 1996; JÜTTNER, 1999

first 20 m from the bank at the different sites were considered to minimize misinterpretation due to dilution by other groundwater. At the study locations Mündelheim, Cologne and Wittlaer approximately 20 %, 20 – 50 % and 50 % EDTA were eliminated, respectively. The corresponding amounts of AOS eliminated were approximately 30 %, 50 % and 40 %, respectively. AOX concentrations were reduced by 30 % at Mündelheim [SONTHEIMER, 1991; BRAUCH ET AL., 2000B]. At the „Böckinger Wiesen" site at a distance of 20 m EDTA, AOX and AOS concentrations were reduced by approximately 15 %, 40 % and 20 %, respectively (Figure 1). By summarizing all presented data, it is shown that EDTA, AOS and AOX were eliminated at the investigated locations within the first 20 m from the bank by approximately 15 – 50 %, 20 – 55 % and 30 – 55 % of the river water concentrations, respectively. From the

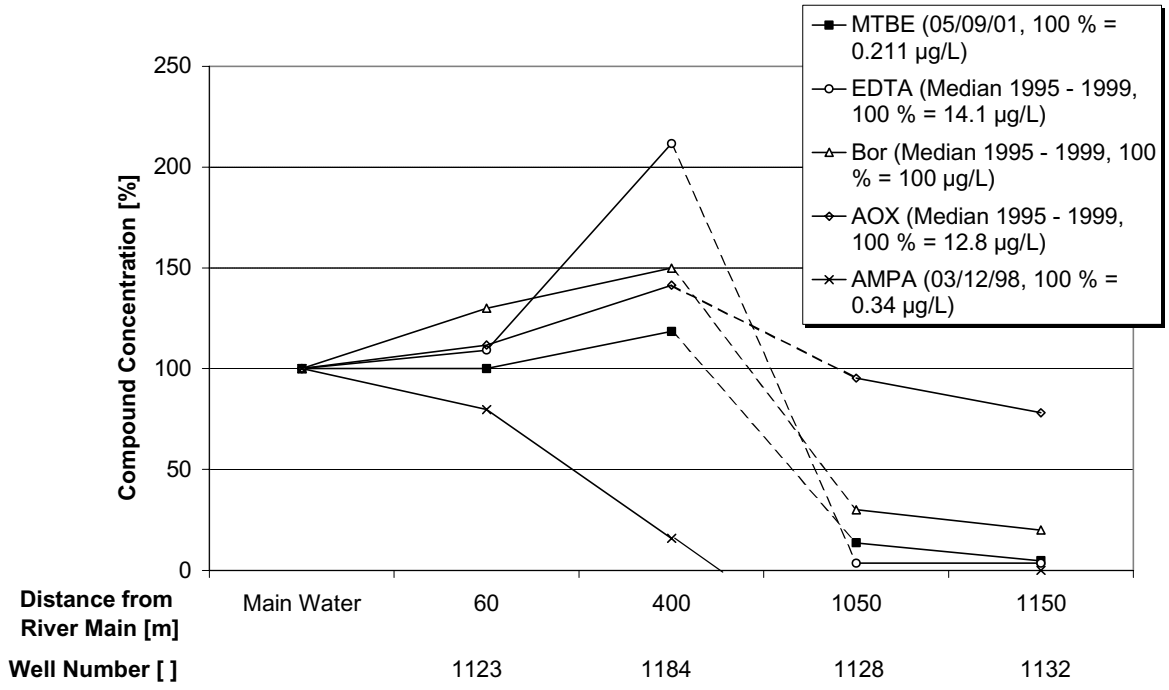


Figure 4-22 Methyl tert-butyl ether (MTBE) concentrations (µg/L) during the riverbank passage at the Lower Main (Hattersheim) in relative comparison (%) to concentrations of ethylenedinitrilotetraacetic acid (EDTA), bor, adsorbable organic halogenated hydrocarbons (AOX), and Aminomethylphosphonic acid (AMPA) [POST ET AL., 1999]. AMPA concentrations were not analyzed in water from well number 1184 but from an adjacent recovering well (ASB1). Dotted lines indicate that to date, bank filtration at Hattersheim only occurs up to about 400 m from the Main river.

limited sample set of this study it can be concluded that MTBE (roughly 25 – 50% elimination of river water concentrations after 20 m) is eliminated to higher amounts than EDTA and in a comparable range or to lower amounts than the AOX and AOS compounds. The MTBE concentrations in recovering well water and raw water at water utility 1 (60 – 120 ng/L) are comparable to published data of 50 – 100 ng/L [BRAUCH ET AL., 2000A]. An elemination rate for MTBE in raw water cannot be calculated as a result of low sample numbers, low concentrations, and the fact that the sampling time of the river water and raw water did not correspond. The amounts of EDTA, AOX and AOS eliminated by bank filtration during transport from Rhine water towards raw water at water utility 1 are 40 %, were 60 – 80 % in 1988 and are 50 – 80 %, respectively [BRAUCH ET AL., 2000B]. From the reported data a decrease in EDTA, AOX and AOS concentrations of roughly 20 % during transport from well A towards raw water due to dilution by groundwater from the land, volatilization or aerobic degradation may be assumed. An eliminated MTBE amount in the range of 45 – 70 % during transport from Rhine water towards raw water of water utility 1 would result if this loss of roughly 20 % during transport from well A towards raw water at the water utility 1 was also assumed for MTBE and added to the amount of about 35 % MTBE loss measured during transport from Rhine water towards well A.

In bank filtration water at the Main river MTBE concentrations were also detected in the trace level range. No conclusions about MTBE attenuation during the riverbank passage can be made as the concentrations were not decreasing but even slightly increasing. Higher MTBE concentrations were measured with increasing distance from the river. Also slightly increasing concentrations of other contaminants were measured. Concentrations of EDTA, bor, and AOX were analyzed in water from the same wells (Figure 4-22). The well known persistent behavior of EDTA and AOX were confirmed at the Hattersheim site. Bor, originating from sewage, is also poorly degradable [RIPPEN, 2000]. Aminomethylphosphonic acid (AMPA) concentrations were not analyzed in water from well number 1184 but from an adjacent recovering well (ASB1). Significant AMPA reduction was observed up to about 400 m from the Main bank [POST ET AL., 1999]. From the analyzed pollutant concentrations at Hattersheim it can be concluded that MTBE is as persistent as other poorly attenuable compounds present in Main water. The slightly increasing concentrations cannot be the result of decreasing pollutant concentrations in Main water, adsorption effects to aquifer materials, fluctuating Main water levels, additional input of contaminants into the groundwater or different sampling techniques and remain unclear. The significantly differing median (211 ng/L) and mean (580 ng/L) MTBE concentrations in Main water in May 2001 are the

result of some exceptional high MTBE concentrations from industrial effluents. The mean concentration should not be used for comparison because it is not representative of MTBE concentrations in river water. Anyhow, shock concentrations can be neglected if bank filtration water is considered as described above.

4.3.6 Conclusions

Traces of MTBE were detected in the drinking water supply at the Lower Rhine site and at Frankfurt/ M in similar concentrations roughly in the range of 50 ng/L. In these regions bank filtration of river water is used for the drinking water production that shows MTBE concentrations roughly in the range of 200 – 250 ng/L [ACHTEN ET AL., 2002B]. The research conducted revealed that traces of the oxygenate were still detectable in riverbank filtered water although MTBE concentrations in water from the Rhine and Main rivers were already in the ng/L range. Neither riverbank filtration nor drinking water processing were able to eliminate MTBE concentrations to a greater extent. The occurrence of point emissions and particularly of non-point emissions of MTBE leading to detectable river water concentrations of the oxygenate should be further monitored in the future as it is a very persistent compound in water, even at low concentrations. Recently, MTBE has been evaluated as „a compound of relevance for waterworks“ [BRAUCH ET AL., 2000A]. Nowadays the presence of MTBE in river water are not of major concern in Germany but concentrations measured in river water show a tendency towards increasing concentrations since 1998 [ACHTEN ET AL., 2002B]. MTBE concentrations measured in drinking water produced from river bankfiltration at the Rhine and Main are often in the range of 50 – 100 ng/L and are approximately 2 - 3 orders of a magnitude lower than the U.S. drinking water standard of 13 µg/L or the odor/ taste threshold of 20 µg/L. However, the results of this study should be evaluated in terms of precautionary aspects as the occurrence of MTBE in environmental waters has already caused major and unexpected concern in some U.S. states. As a result, Northern European countries like Denmark are planning to increase prices for super premium gasoline. If the amount of MTBE used in German gasoline increases significantly as proposed by DEWITT COMPANY [DEWITT COMPANY, 1998 AND 1999] to meet gasoline requirements of reduced aromatic compounds, environmental concentrations of the oxygenate will soon be close to the same order as measured in California or New Jersey. The persistent behavior of MTBE will lead to measurable environmental amounts for years, even if its use is reduced soon.

5 COMPARTMENT MODELING OF MTBE IN THE GENERIC ENVIRONMENT AND ESTIMATIONS OF THE AQUATIC MTBE INPUT IN GERMANY USING THE EQC MODEL

5.1 Abstract

The behavior of methyl *tert*-butyl ether (MTBE) in the two most relevant compartments water and air in the generic environment and in a simulated German environment is investigated using the equilibrium criterion (EQC) model. Due to lack of literature data, the half-life time of MTBE in river water is estimated to about 80 – 120 d (105 d) at 18 °C and roughly 1.5 y (533 d) at 4 °C from a batch experiment. The EQC model considers four compartments, air, surface water, soil and sediment in an environment of typically 100,000 km² with about 10 % of the area covered with water. The user can progress through the tiered sequence of Level I - III with increasing complexity which reveal more information about the fate of the considered chemical. The equilibrium mass distribution of MTBE calculated with the Level I model shows that 87 % partition into air and 13 % into surface water at 10 °C. The results of the Level II calculations indicate that 50 % of MTBE in the air is transported from the system and 38 % is degraded at 10 C. The total persistence time of 3 d is little lower than that calculated for alkylbenzene sulfonates. The MTBE input into water is significantly more sensitive to the "mode of entry" than input into air. The MTBE concentration in surface water is almost exclusively the result of direct emission into water, whereas the atmosphere can additionally be loaded by volatilization from water. For the estimation of the aquatic MTBE emission and average MTBE concentration in surface water in Germany, 20 – 80 kg/a (50 kg/a) and 50 ng/L are very roughly assumed, respectively. Under the conditions of the model (e.g. 10 % water surface), neither measured MTBE concentrations of the oxygenate in waste water and industrial effluents nor estimated loss of industrial used MTBE in Germany explain the estimated surface water concentration. For the year-round scenario at 10 °C, MTBE concentrations of 19 ng/L (surface water) and 167 ng/m³ (Air) result. The amount of 19 ng/L is too low compared to the estimated average of 50 ng/L. The water surface in Germany of 2.2 % instead of 10 % as used by the model will at least partially contribute to slightly higher concentrations. However, it still remains unclear, if the assumptions of the model, the lack of analyses from industrial effluents or both are responsible for the difference. Additional aquatic emission sources could result from further industrial effluents, gasoline transport on and storage near rivers.The comparison of winter and summer scenarios shows

that in summer, atmospheric (25 %) and aqueous (50 %) concentrations are lower than in winter due to higher degradation rates.

5.2 Introduction

The use of the oxygenate methyl *tert*-butyl ether (MTBE) has led to significant groundwater contamination in the U.S.. Major concern is about drinking water quality due to leakage from underground storage tanks (LUSTs) of oxygenated gasoline because MTBE concentrations in the mg/L range were reported for such locations [HAPPEL ET AL., 1998; BRUCE AND MCMAHON 1997; EFFENBERGER ET AL., 2001]. Since the 70s – 80s, MTBE has spread all over the aquatic and atmospheric environment and concentrations in the ng/L range were reported for countries that use it as octane enhancer and/ or smog reducer [DELZER ET AL, 1996; REISER AND O'BRIEN, 1998; BENDER ET AL., 2000; BAEHR ET AL, 2001; ACHTEN AND PÜTTMANN, 2000; ACHTEN ET AL., 2001A, 2002A AND B]. Vehicle engines running with oxygenated fuel seem to represent the main sources of these widely spread low-level concentrations [FRASER ET AL., 1998; ACHTEN ET AL., 2002B].

Although many physico-chemical properties of MTBE are well known and are subject of current research [BIERWAGEN ET AL., 2001], little information has been published so far about the behavior and distribution of MTBE between the different compartments air, water, soil and sediment [PAHLKE ET AL., 2000; MEF, 2001; SQUILLACE ET AL., 1995]. Under equilibrium conditions, a partitioning of MTBE of 94 % into air, 6 % into surface water, 0.054 – 0.07 % into soil and 0.001 – 0.08 % into sediment has been reported [PAHLKE ET AL., 2000; MEF, 2001]. The steady-state mass balance calculated with another model by Environment Canada for Southern Ontario showed a MTBE distribution of 56 % in air and 42 % in surface water [SQUILLACE ET AL., 1995]. Continental MTBE concentrations for Europe in the atmosphere and in surface water calculated with the model EUSES were 220 ng/m³ and 100 ng/L, respectively [MEF, 2001].

For the evaluation of the MTBE situation in Germany, the amount of MTBE released into the environment, the partitioning between the different compartments and the degradation are important. In this study, the environmental fate of MTBE is estimated and evaluated by use of the equilibrium criterion model (EQC, Level I - Level III). In the first step, the general distribution behavior of MTBE is considered (Level I). In the second step, concentrations in the most important compartments atmosphere and surface water are estimated for scenarios with varying temperatures resembling year-round, summer and winter conditions. By use of

the Level III model, the sensitivity of different emissions into atmosphere, surface water, soil and sediment can be characterized with respect to the environmental concentrations of the ether. Due to a lack of literature data, the degradation rate of MTBE in river water had to be estimated in a batch experiment to allow an evaluation of the relevance of this process.

5.3 Batch Experiment

The degradation of MTBE in river water was investigated at 4° C and 18 °C using fresh water samples taken from the Main on 08/23/00. The samples could be stored in the dark since photolysis of MTBE in water is not an important removal process [MEF, 2001]. Aliphatic ethers do not absorb light at wavelengths >290 nm and the UV-spectrum indicates that direct photolysis may not occur. Two aliquots of a Main water sample (1 L) collected at Frankfurt/ M city on 08/23/00 were filled into 100 mL brownglass bottles (without headspace) and kept in the dark for 50 weeks. The bottles were regularly probed (n = 24) and analyzed for MTBE. By this procedure, the sample volumes in the bottles were continuously reduced increasing the headspace volume. For data analysis, the resulting concentrations in the water phase were corrected for evaporation losses assuming equilibrium conditions.

5.4 The EQC Model

The equilibrium criterion model is an evaluative multimedia model based on the fugacity concept [MACKAY, 2001]. The fugacity approach was introduced as a more convenient thermodynamic equilibrium criterion than chemical potential and can be understood as the effective vapor pressure. The EQC model considers four compartments: air (bulk, air phase, aerosol), surface water (bulk, water phase, suspended sediment phase, fish phase), soil (bulk, air phase, water phase, solid phase) and sediment (bulk, water phase, solid phase) [MACKAY ET AL., 1996A]. Calculations are carried out for a generic environment of a fixed area of typically 100,000 km² with about 10 % of the area covered with water [MACKAY, 1991]. Default values for the compartment depths are 1000 m (air), 20 m (water), 0.1 m (soil) and 0.01 m (sediment). Thus, the model refers to volumes of 100,000 km³ (air), 200 km³ (water), 9 km³ (soil), 0.1 km³ (sediment), 0.001 km³ (suspended sediment) and 0.0002 km³ (fish) [MACKAY ET AL., 1996A]. Homogeneous compartment structures are assumed. The equations

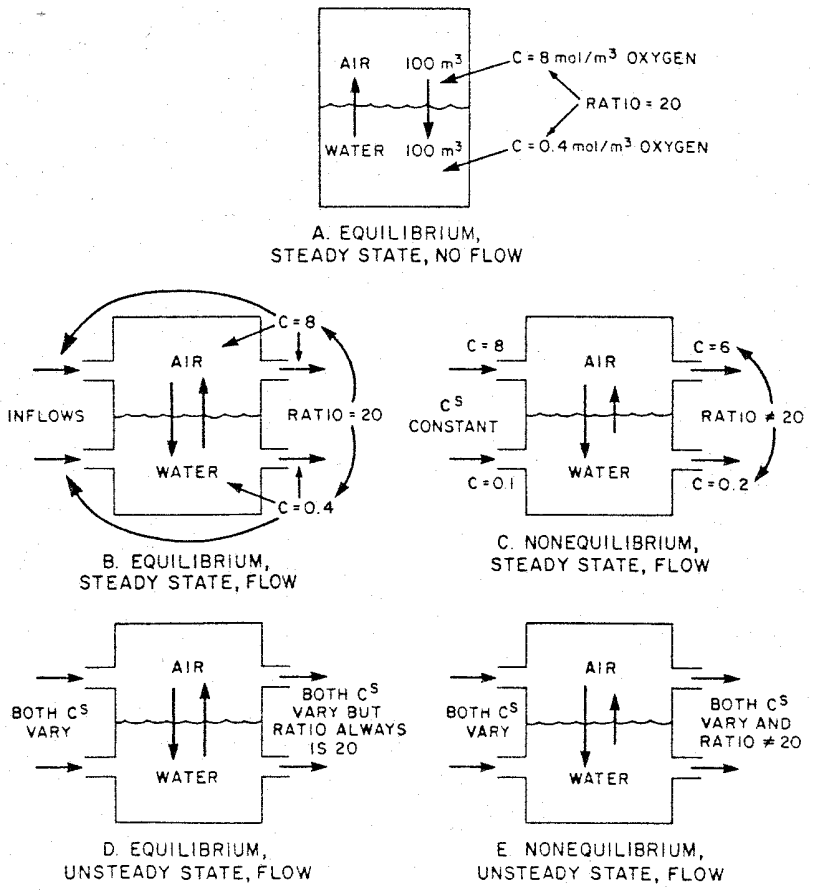


Figure 5-1 Illustration of the equilibrium and steady state conditions characterizing a) Level I, b) Level II c), Level III and d, e) Level IV using the example of oxygen concentrations partitioning into water and air. Equilibrium implies that the oxygen concentrations in air and water achieve a ratio or partition coefficient of 20. Steady state implies unchanging with time, even if flow occurs and regardless of whether equilibrium applies or not [MACKAY, 2001].

used to describe partitioning, transport, and transformation processes as well as the input parameters and their default values used by the model are described elsewhere [MACKAY ET AL., 1996A AND B, MACKAY ET AL., 1995]. The EQC model allows the user to progress through the tiered sequence of Level I, II and III (and possibly IV) models, which have increasing complexity and data requirements, and progressively reveal more information about the environmental fate of the considered chemical. General distribution of a chemical into the compartments air, water, soil and sediment is described by the static equilibrium

Level I model (a) (Figure 5-1). Degradation and transport processes are additionally considered by the steady-state and equilibrium Level II model (b). Here, a constant emission of the pollutant is assumed which is instantaneously partitioned into all compartments according to the equilibrium assumption. In Level III calculations (c, steady-state and non-equilibrium), compartment specific emissions can be defined and the exchange rates between the different compartments are now taken into account due to the non-equilibrium assumption. Different concentrations over time (d and e, unsteady state) are not considered in this study.

According to the properties of the considered chemical, the compound has to be assigned to one of three defined categories [MACKAY ET AL. 1996A]. The properties of type 1 chemicals allow the distribution in all compartments which is observed for most organic compounds (e.g. chlorobenzene, hexachlorobenzene, polychlorobiphenyls, etc.). Type 2 chemicals are not measurable in the air but possibly in all other compartments (e.g. cations, anions and involatile organic compounds). Substances not to be found in the water compartment but possibly in all other phases belong to the type 3 category (very hydrophobic compounds, e.g. long-chain hydrocarbons, silicones and polymers).

5.5 Model Design for MTBE

5.5.1 Physico-Chemical Data

MTBE has to be considered as a type I chemical possibly occurring in all phases. Its molecular weight is 88.15 g/mol, and the melting point is –108.6°C [MEF, 2001]. For the modeling, log K_{OW}, water solubility and vapor pressure are the most important physico-chemical properties. The influence of the log K_{OW} on the results was checked with the Level I model. Simulation results using a log K_{OW} of 0.94 were compared to a second scenario with a slightly higher log K_{OW} of 1.06 [MEF, 2001] showing a relative small relevance of this parameter. In all other scenarios 0.94 was used as log K_{OW}.

Water solubility and vapor pressure were varied according to the temperature chosen for the respective scenario as there were year-round (10 °C), summer (20 °C) and winter scenarios (4 °C) performed. Additionally, the half-life times in air and water were adapted to represent annual mean, summer or winter conditions, respectively. The data used for the calculations are summarized in Table 5-1. All environmental parameters not explicitly mentioned were

Table 5-1 Water solubility, vapor pressure, half-life times in air [MEF, 2001] and in water of methyl tert-butyl ether (MTBE) at 4, 10 and 20°C used in modeling for year-round, summer and winter scenarios.

Scenario	Temperature	Water Solubility	Vapor Pressure	Half-life time Air	Half-life time Water
	[°C]	[g/l]	[hPa]	[d]	[d]
Winter	4	70	ca. 150	7	no degradation
Year-round	10	51	ca. 185	5	ca. 315
Summer	20	42	268	3	ca. 105

used as set by default in the model. Effects of hydrology, meteorology, proportion of the media, composition of water or soil and temporal changes are not included.

5.5.2 Emission Rates and Degradation Half-Life Times

For Level I considerations, a fixed emission of 100 t into the system was assumed. For Level II calculations, the emission rate was fixed to 1000 kg/h and half-life times of MTBE in the atmosphere ranging from 3 d (summer scenario) to 6 d (winter scenario) [WALLINGTON ET AL., 1988; SMITH ET AL., 1991] were used. Degradation half-life times in the aqueous phase have been estimated in the batch experiment ranging from no degradation (4°C, winter) to 105 d (20 °C, summer).

For Level III calculations, a total emission rate of 2285 t/a MTBE into German air [PAHLKE ET AL., 2000] was used. The emission rate into surface water in Germany was roughly estimated to be in the range of 20 - 80 t/a and a mean value of 50 t/a was used.

5.6 Results

5.6.1 MTBE Degradation in Water from Main River

The persistence of MTBE in a Main water sample was investigated at two different temperatures (4 °C and 18 °C). The MTBE concentration at the sampling day was about 220 ng/L. The results of the batch experiments are presented in Figure 5-2. The eliminating

factors include volatilization and biotic degradation. Abiotic degradation is not an important removal process, since MTBE is resistent to hydrolysis within environmentally relevant pH scale [MEF, 2001]. However, under acidic conditions (pH $\leq$2), MTBE is sensitive to hydrolysis which could be relevant for contaminated groundwater [O'REILLY, ET AL., 2001]. The UV-spectrum indicates that photolysis may not occur in water, as aliphatic ethers do not absorb light at wavelengths >290 nm [MEF, 2001]. Biotic degradation is assumed to be mainly responsible for the observed MTBE loss during the batch experiment. After a lag-phase, significant decrease in MTBE concentrations occurred during 43 – 107 d (18 °C) and in the interval of 69 – 107 d (4 °C) after the start of the experiment. After 107 d, amounts of 53 % (18° C) and 23 % (4° C) were eliminated. During the following weeks, MTBE was

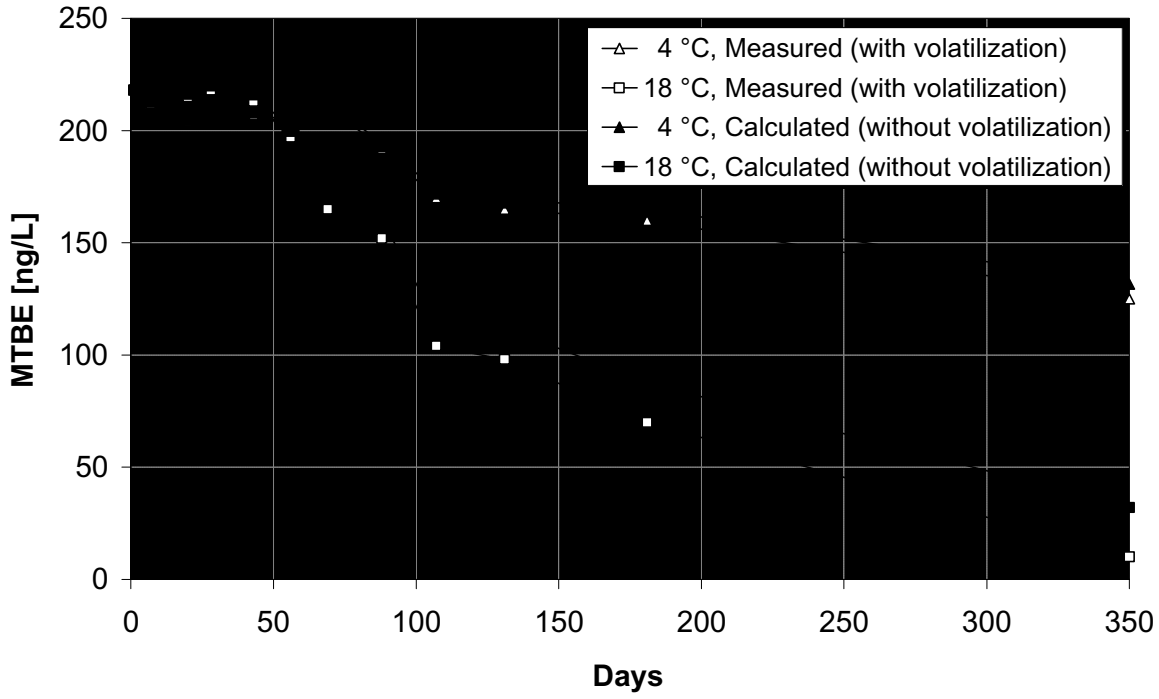


Figure 5-2 Methyl tert-butyl ether (MTBE) concentrations (ng/L) in a Main water (08/23/00) sample observed within a time interval of 350 d at 4 °C and at 18 °C. Volatilized amounts during the experiment were calculated under the conditions of equilibrium and tieredly changing volumina of the gasphase and aqueous phase. They were substracted from measured MTBE concentrations (black symbols). The reduction of the resulting MTBE concentrations over time is probably assigned to biodegradation. Data points with larger symbols were used for the calculation of half-life times.

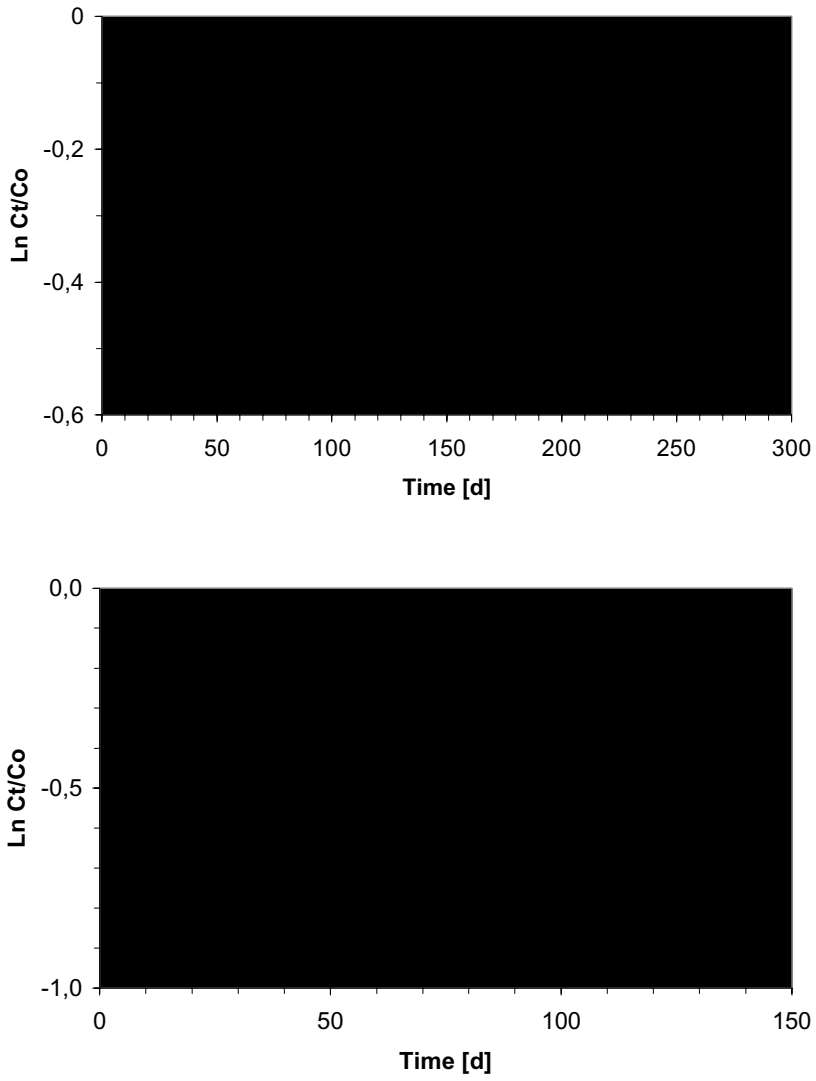


Figure 5-3 Logarithmic regression of methyl tert-butyl ether (MTBE) concentrations assumed to represent biodegradation. The data originate from the batch experiment at 4 °C (top) and 18 °C (bottom). Half-life times of 105 d at 18 °C and 533 d at 4 °C result using first order kinetics.

eliminated only slowly at both temperatures. Finally, after 350 d, MTBE was not detected in water stored at 18 °C and about 50 % of the initial MTBE concentration was still measured in Main water stored at 4 °C. As volatilization of MTBE during the experiment is likely to occur due to the increasing headspace volume, its influence was estimated assuming equilibrium conditions. After 350 d, volatilized amounts of only 3 % (4 °C) and 10 % (18 °C) of the initial MTBE concentration were calculated. Logarithmic regression of the data at both temperatures are shown in Figure 5-3. For the assumed biodegradation, half-life times of 105 d at 18 °C

and 533 d at 4 °C were calculated using first order kinetics. Cometabolic degradation possibly occurring during the lag-phase is neglected. The results of these batch experiments, however, represent only very rough estimations. Due to the limited amount of substrates the microorganisms probably adapted to MTBE leading to a faster MTBE degradation in the laboratory than it would take place in natural river water. However, the half-life times received from the batch experiment were used for best-case and year-round calculations. No degradation was assumed as worst case in winter time.

5.6.2 Modeling of MTBE in the Generic Environment by the EQC Model

5.6.2.1 Level I Calculations

The equilibrium mass distribution of MTBE calculated with the Level I model is shown in Figure 5-4. The amounts that partition into soil and sediment range from 0.0014 - 0.135 % and from 0.0001 - 0.003 %, respectively, and are neglected for future considerations. It can be seen that the partitioning of MTBE is shifted more towards the air compartment with increasing temperature. This is due to the increase of the vapor pressure and the resulting Henry coefficient. The resulting data from a second scenario run with a log K_{OW} of 1.06 do not differ significantly.

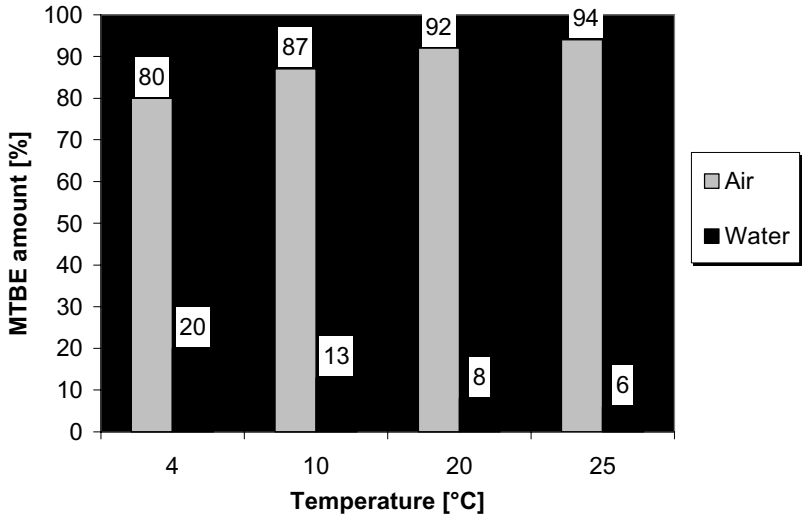


Figure 5-4 Equilibrium mass distribution of methyl tert-butyl ether (MTBE) calculated by the Level I model.

5.6.2.2 Level II Calculations

The results of Level II calculations with a total fixed emission rate of 1000 kg/h are dominated by the air compartment. This is due to the equilibrium assumption leading to a similar mass distribution as with Level I. The reactive loss in the atmosphere is calculated to about 38 % (? 9 %), whereas only 0 – 2.8 % are degraded in water. The advective transport out of the system of atmospheric and aquatic MTBE amounts are 50 % (? 16 %) and 1 % (? 0.6 %), respectively. The total persistence time in the system varies depending on the different atmospheric half-life times and is 2.9 d (? 0.6 d). The sensitivity of the aquatic half-life time is negligible which is also observed in Level III calculations (Figure 5-5).

5.6.2.3 Level III Calculations in the Generic Environment

With the Level III model, different emission scenarios with mean year-round environmental conditions have been calculated using inputs of (a) 1000 kg/h into air only, (b) 950 kg/h into air and 50 kg/h into water, (c) 500 kg/h into both air and water and (d) 1000 kg/h into water only. The results are summarized in Figure 5-5**.** It can be seen that the amount emitted into each compartment has a significant influence on the steady-state mass distribution in the generic environment. It is also shown that the concentration in water is much more sensitive to the "mode of entry" than the atmospheric MTBE concentration. The concentration of the oxygenate in surface water (for example at emissions of 1,000 kg/h into each compartment air and water resulting in 404,000 kg) is almost exclusively (98.5 %) the result of direct emission into water (398,000 kg at an emission of 1,000 kg/h into water only), whereas the atmosphere is additionally loaded by volatilization from water (35,832 kg at an emission of 1,000 kg/h into water only, Table 5-2).

5.6.3 Estimations of the MTBE Amount Emitted into Surface Water and the Average Surface Water Concentration in Germany in 1999/ 2000

5.6.3.1 Amount of MTBE Emitted into German Surface Water

In a first approach to estimate MTBE emissions into surface water in Germany, the following assumptions were made: (1) Public waste water in Germany sums up to $9.8*10^9$ m³/a with an average concentration of 150 ng/L giving a total emission of 1.5 t/a MTBE. (2) Industrial

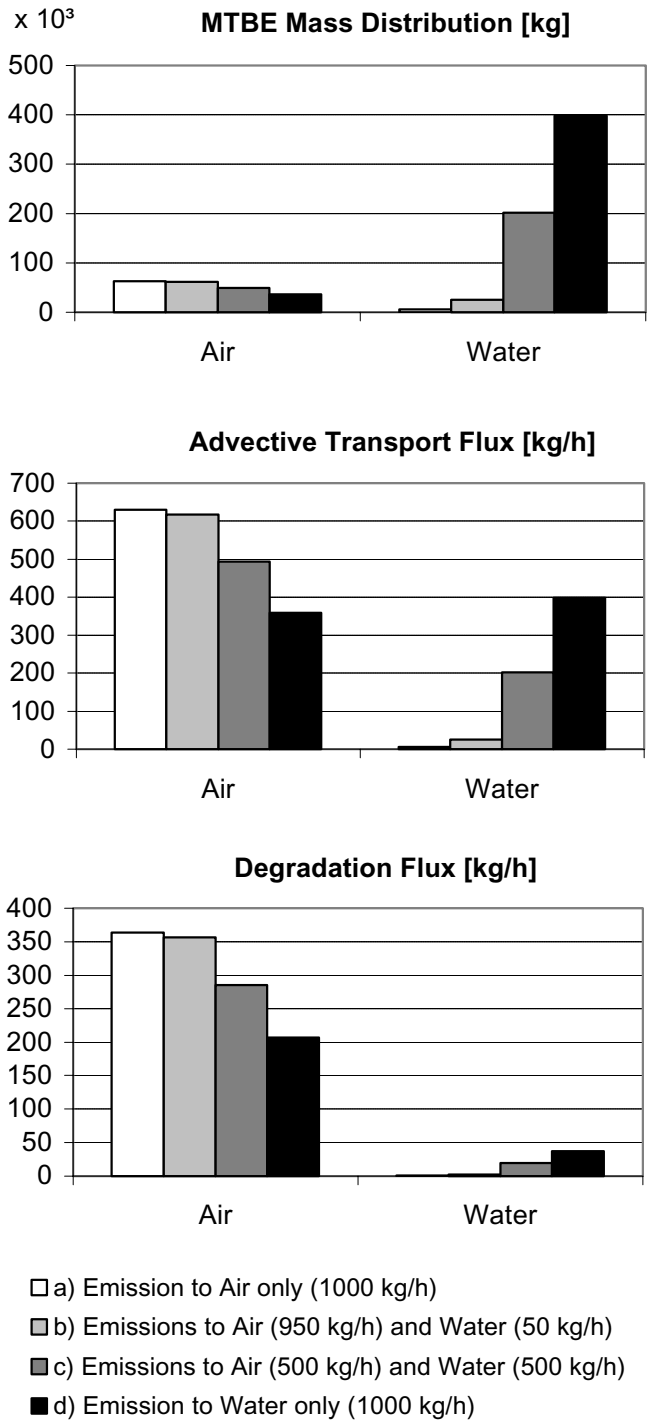


Figure 5-5 Results of four different Level III emission scenarios for methyl tert-butyl ether (MTBE): a) 100 % emission into the air, b) 95 % emission into air and 5 % emission into water, c) 50 % emission into air and water each and d) 100 % emission into water in generic the environment. Year-round conditions were used that are described in Table 5-1.

Table 5-2 Amounts of methyl tert-butyl ether (MTBE) in air (ng/m³) and water (ng/L) depending on single and multiple emissions using the Level III model in the generic environment and year-round conditions.

Emission medium and rate of emissions [kg/h]	Amount at steady state [kg]	
	Air	Water
Air (1,000)	63,018	5,398
Water (1,000)	35,832	398,000
Air (1,000) and Water (1,000)	98,849	404,000

effluents (sum: $1.7*10^9$ m³/a) are divided into a low-contaminated fraction (90%) and a high-contaminated one (10 %) assuming concentrations of 50 ng/L and 20,000 ng/L MTBE, respectively [ACHTEN ET AL., 2002B; UBA AND SB, 1999]. The total input into German surface water then calculates to 6.5 t/a. In a second approach, an aqueous emission rate of 9 t/a was estimated assuming a loss of 0.1 % of industrially used MTBE in Germany (7500 t/a in 1999) [MEF, 2001] and adding the above mentioned amount of 1.5 t/a from public waste water. However, emission rates of 6.5 – 9 t/a into German surface water seem too low if it is considered that, for example, an MTBE emission of 1.9 t/a into the river Rhine by a single company is reported for 1998 [BASF, 1999]. It can well be assumed that the industrial loss is significantly higher than 0.1 % and additonal MTBE sources are not yet considered in this calculation.

As most (98.5 %) of the total MTBE amount consumed (500,000 t in 1999) is used in gasoline [MEF, 2001] losses during transport, filling and storage seem likely. This assumption is supported by results from Rhine water samples (n = 23) in the area from Schaffhausen to Wesel collected within two days in November 2000. The highest MTBE concentration of 383 ng/L was measured at Leopoldshafen near Karlsruhe where several refineries and one of the main producers of MTBE in Germany are located near the Rhine. Contaminated groundwater resulting from leaking underground storage tanks (LUSTs) dewatering into rivers could also pay a contribution, which has not yet been investigated.

In a final approach, based on the considerations made above, an estimated loss of 0.01 % of the total amount consumed in Germany was used to estimate a surface water emission rate of 50 t/a in 1999, which was then used in the EQC model calculations.

5.6.3.2 Average Surface Water Concentration in Germany

MTBE concentrations in German surface water vary from not detected (<10 ng/L) to more than 2000 ng/L [ACHTEN ET AL., 2002B; BRAUCH ET AL., 2000A; EFFENBERGER ET AL., 2001]. Rivers used by ship traffic and urban creeks with industrial influence often show concentrations in the range of 100 – 300 ng/L, whereas generally lower concentrations (about 10 – 50 ng/L) are detected in rural creeks (Table 5-3) [ACHTEN ET AL., 2002B]. From the data,

Table 5-3 Average concentrations of methyl tert-butyl ether (MTBE) in German surface water. The detection limit is 10 ng/L and it was used for calculations of average concentrations if MTBE was not detected. On the basis of the results of the analyses, the upper and lower Rhine was separated at Karlsruhe for simplification. [ACHTEN ET AL., 2002B, BRAUCH ET AL., 2000A, EFFENBERGER ET AL., 2001]

Surface water	Average MTBE concentration [ng/L]
Upper Rhine	90
Lower Rhine	250 - 300
Upper Main	25
Lower Main	150 - 200
Elbe	not calculated (analyzed samples range from 30 - 470 ng/L)
Neckar	160
Weser	130
Danube	not detected
Small rivers	not calculated (analyzed samples range from not detected - 200 ng/L)
Rural creeks	20
Urban creeks	50 - 250
Channels	80
Sewage plant effluents	100 - 250
Industrial effluents	70, with some exceptional high concentrations up to 30 000
Urban runoff	100-200
German surface water (roughly estimated)	50

an overall average MTBE concentration in German surface water can hardly be estimated. However, an attempt is made and a mean concentration of 50 ng/L is proposed for the years 1999/ 2000.

5.6.4 Level III Simulations of MTBE Using the Estimated German Emission Scenario

It has been shown that it is hardly possible to estimate the total input and the concentration of MTBE in German surface water on the basis of the available data. However, a total emission rate of 2285 t/a MTBE into air [PAHLKE ET AL., 2000] and of 50 t/a into surface water can be used as a first approximation. With these data, year-round (10 °C), summer (20 °C) and winter scenarios (4 °C) are performed (Table 5-1). In the year-round scenario, MTBE concentrations of 19 ng/L (19 % of total mass) in water and 167 ng/m³ (81 % of total mass) in

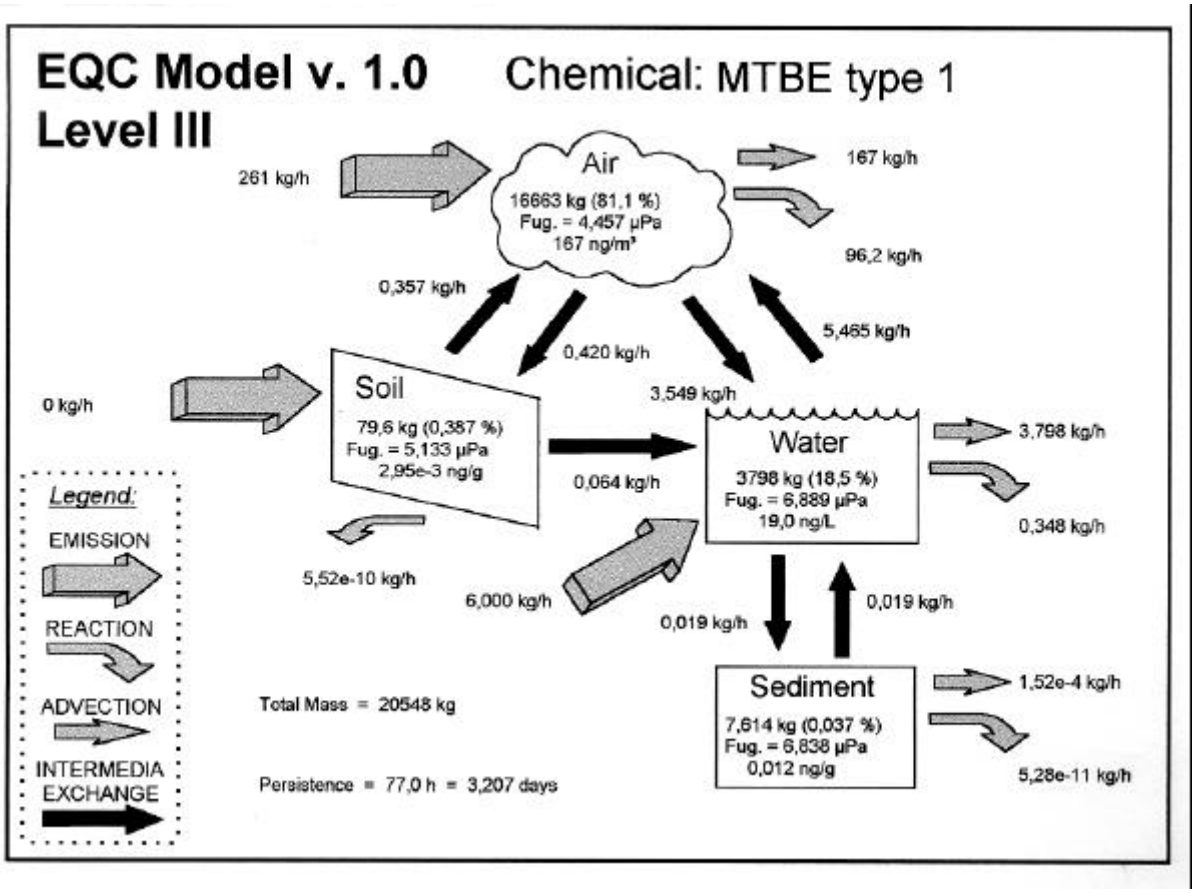


Figure 5-6 Year-round scenario of concentrations of methyl tert-butyl ether (MTBE) in Germany in 1999/ 2000. The used data are described in the section model design.

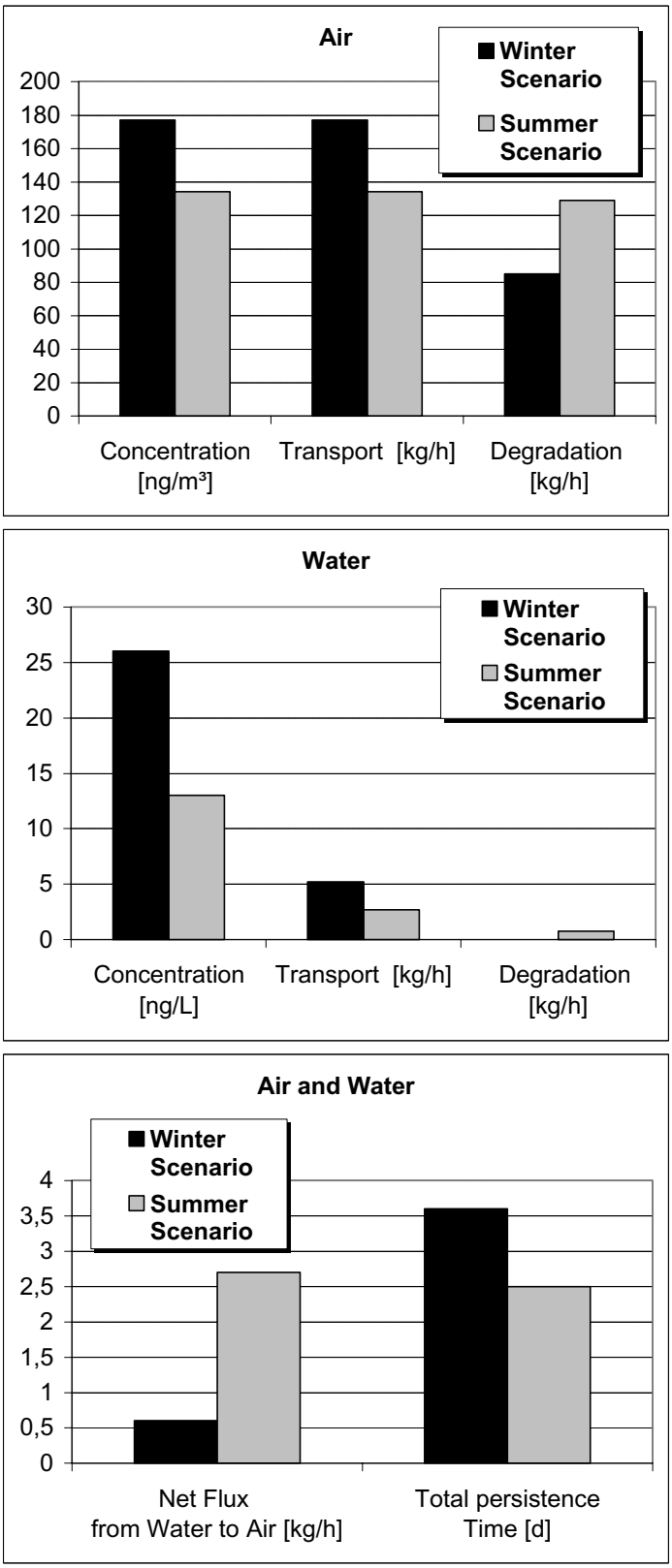


Figure 5-7 Comparison of the Level III results from the winter and summer scenarios for methyl tert-butyl ether (MTBE) with the estimated German emission scenario.

air result (Figure 5-6). The compartments soil and sediment can be neglected. The degradation flux in the atmosphere is calculated to 96 kg/h, whereas only 0.4 kg/h are degraded in water. The advective transport of MTBE out of the system is 167 kg/h for the atmosphere and 3.8 kg/h for water. In both compartments, calculated MTBE loss by advective transport is significantly higher than by degradation. The net flux between the two compartments of 2 kg/h from water to air is comparably low. The calculations are repeated assuming different temperatures simulating winter and summer time. The results are summarized in Figure 5-7. In summertime, the calculated steady-state MTBE concentration in water is only half of the value for wintertime. This is due to the changes in water solubility and vapor pressure as well as the different half-life times. The varying MTBE partitioning and degradation behavior is responsible for the difference at about the same amounts. In the atmosphere, the concentration in summer is only about 25 % lower than in wintertime which is the result of higher OH- radical concentrations compared to winter. MTBE degradation in the atmosphere almost equals transport out of the system in summer, whereas in winter the degradation flux is only half of the advective flux. In the water compartment, transport is dominating degradation by far in winter and even with the 50 % reduction calculated for summer transport is still about three times higher than degradation. The net MTBE flux between the compartments water and air is low and varies from 0.6 kg/h (winter) to 2.7 kg/h (summer). The total persistence time of MTBE in the system shows a relatively small variation ranging from 2.5 d (summer) to 3.6 d (winter).

5.7 Discussion

5.7.1 General Aspects of the Behavior of MTBE in the Environment

MTBE is expected to be fairly persistent in Main water as half-life times of about 80 – 120 d (105 d) at 18 °C and roughly 1.5 y (533 d) at 4 °C have been calculated from the batch experiment. This is supported by the above-mentioned domination of transport over degradation in the water compartment. The volatilization should also be low considering calculated half-life times of 4 – 8 d from Rhine and Main water and of 1 – 3 d from creeks in wintertime using the data published by PANKOW ET AL. [1996] for MTBE volatilization from river water. The equilibrium mass distribution of MTBE calculated with the Level I model of 94 % in air and 6 % in water at 25 °C are the same as calculated elsewhere [PAHLKE ET AL, 2000; MEF, 2001]. However, for environmental considerations, the average annual

temperature should be taken into account and partitioning of 87 % in air and 13 % in surface water at 10 °C seems more representative. The results of the Level II calculations show that atmospheric MTBE transport could be an important mechanism as only 38% of the atmospheric MTBE are calculated to be degraded within the system, whereas 50% leave the system by advection. This is also supported by the detection of MTBE in the atmosphere of some U.S. states with no known MTBE usage [CLAWGES ET AL., 2000]. However, in Germany, the oxygenate was not detected in precipitation in remote areas in wintertime, whereas it was often detectable in urban air [ACHTEN ET AL., 2001A]. The general total persistence time of 2.9 d for MTBE is little lower but comparable to the value of 4 d calculated for linear alkylbenzene sulfonates (LAS) with the Level II model [MACKAY ET AL., 1996B]. From considerations of MTBE in the generic Level III environment, it can be concluded that water concentration is significantly more sensitive to the "mode of entry" than air concentration. This effect is mainly the result of the high water solubility and low aqueous degradation properties of the oxygenate. The calculated contribution of 98.5 % of MTBE in the water compartment originating from direct emission into water emphazises the significance for the investigation of sources emitting the oxygenate directly into river water. On the other hand, MTBE concentrations in air are affected by both, direct emission and volatilization from water.

5.7.2 MTBE Concentrations Calculated by the Level III EQC Model with German Emission Scenario in Comparison to Measured Data (1999/ 2000)

Under the assumptions of atmospheric (2285 t/a) and aqueous emission rates (50 t/a), the average MTBE concentration in German surface water in 1999/ 2000 of approximately 50 ng/L is more than twice as high as the mean surface water concentration of 19 ng/L calculated by the EQC model in the year-round scenario. This difference could be explained by some fixed model parameters which are not adequate for the German situation. The fixed amounts of 10 % of the area covered with water, a water volume of 200 km³ and a water depth of 20 m do not represent the situation in Germany. Here, the amount of 2.2% area [STATISTISCHES BUNDESAMT, 2001] covered with water and an estimated water depth of 1.35 m may be more realistic resulting in higher MTBE concentrations than calculated by the model. Another reason for the difference could be an overestimated average MTBE concentration in German water. Finally, only a low sample amount of industrial effluents with some exceptional high MTBE concentrations were analyzed and additional unknown

industrial input cannot be taken into account due to the lack of analytical data. In Europe, where the MTBE use (2,646,000 t/a) was about 5 times higher compared to Germany (500,000 t/a) in 1999, the calculated continental MTBE concentration in water of 100 ng/L [MEF, 2001] would be higher by factors of 2 or 5.

Data of atmospheric MTBE analyses in Germany have not been published. The calculated average concentration of the oxygenate in European air of 220 ng/m³ is higher by a factor of 1.3 compared to the result of this study for German air of 167 ng/m³.

MTBE is hardly degradable in water and for winter- and year-round scenarios, the assumption of slow degradation or no degradation does not have a significant influence on the resulting environmental concentrations.

The results of the comparison of the winter and summer scenarios show that the behavior of MTBE varies significantly. In summer, atmospheric (25 %) and aqueous (50 %) concentrations are lower than in winter which is the result of higher degradation rates (and lower water solubility). As a consequence, in winter, more MTBE remains undegraded and is transported. Volatilization of MTBE from water is the dominating pathway between the two compartments throughout the year.

5.8 Conclusion

The results show that a part of emitted MTBE into the environment partitions into the aquatic compartment, which should not be neglected. Additionally, a significant temperature dependence of environmental MTBE concentrations with higher amounts in winter were observed.

One of the most sensitive parameters in modeling the environmental fate of organic compounds is the emission of the substance into the various compartments. Direct MTBE emission into water, for example, has proved to be a very sensitive parameter for MTBE concentration in surface water. Estimations on the basis of available production volumes and use patterns together with measured MTBE concentrations in waste water and industrial effluents cannot fully explain the mean surface water concentrations calculated from single measurements in Germany.

Additional industrial effluents, losses from gasoline distribution or storage tanks, emissions from tank ships and shallow urban groundwater contaminated with MTBE dewatering into near rivers could represent additional possible emission sources. More research is needed to detect such sources that in many cases might be point-source emissions.

6 CONCLUSIONS AND FUTURE IMPLICATIONS

By use of the presented methods, MTBE can be analyzed in gasoline by GC/ FID with a single capillary column and in water at low levels using HS-SPME/ GC-MS. The second method allows to measure aqueous concentrations of MTBE in river water and precipitation at levels as low as 10 – 50 ng/L. These values often occur in German environmental samples and can be detected with a relative standard deviation of 10 - 11 %. The method is also suited for the measurement of other oxygenates and VOCs in water. Aqueous samples with concentrations of MTBE and BTEX in the µg/L - mg/L range, as often occur at contaminated sites, have to be diluted before analysis and matrix effects need to be considered.

MTBE will probably persist in the environment for several decades to come. Today, MTBE represents besides chlorinated hydrocarbons like chloroform, trichloroethene and tetrachloroethene the quantitatively dominating organic compounds in river waters. In the U.S., air quality has improved at the cost of drinking water contamination and of ubiquitously dispersed MTBE concentrations at low levels nationwide. As a consequence, high financial expenditure for research and remediation techniques are necessary. In Germany and elsewhere in Europe, MTBE has also been detected in the atmospheric and aquatic environment although it is generally used at lower amounts compared to some states of the U.S.. MTBE concentrations in the Main and Rhine rivers were lower by about a factor of two compared to streams e.g. in New Jersey. In 1999/ 2000, effluents of chemical industry represent significant point-source emissions for German river water. Due to the unfavorable physico-chemical properties, direct MTBE emissions into water is a very sensitive parameter compared to other emission pathways and only small amounts released result in measurable concentrations over long distances because it is very persistent in water. All emission sources linked with the production, transport and use of oxygenated gasoline are responsible for lower but well dispersed concentrations of the oxygenate in the aquatic environment, that are mostly collected by surface runoff. For Germany, a total emitted MTBE amount of roughly 50 t/a into the aquatic environment and a mean surface water concentration of 50 ng/L are estimated for 1999/ 2000. Under the assumptions of atmospheric and aqueous emission rates of 2285 t/a and 50 t/a, respectively, a calculated mean MTBE concentration in German water of 19 ng/L (at 10 °C) results using the EQC model. The difference of the estimated average MTBE

concentration of 50 ng/L and the calculated amount of 19 ng/L in German water remains unclear. However, the fixed amount of 10 % water surface in the model is at least partially responsible because the water surface in Germany is only 2.2 % leading to higher concentrations. The occurrence of industrial MTBE emissions that can show concentrations as high as 30 µg/L, are mostly unknown. After 15 years since the introduction of the oxygenate in Germany, the compound can be detected in urban precipitation in wintertimes and in surface waters with a tendency towards increasing concentrations. This distribution is generally not desirable and is also of concern as MTBE is detected at low levels in drinking water produced from riverbank filtration. The amounts represent trace-level concentrations and to nowadays knowledge are not of health concern as they remain 2 – 3 orders of a magnitude below the drinking water standard of the U.S. of 13 µg/L but they are important for precautionary aspects. Due to limited data, the toxicity of the oxygenate should not be finally evaluated.
The MTBE use and concentrations in the environment are increasing and will probably be even higher in the future. As a result from the directive limiting aromatic hydrocarbons in gasoline to 35 % (w/w) from 2005 on, in the future increased amounts of oxygenates will be needed to guarantee the required octane numbers. If only MTBE is used for this purpose, in Europe, a doubling of the used amout can be expected from 2005 on which would be still by a factor of 2 -3 below the Californian situation except for large rivers where a comparable situation in Germany and California would be reached soon.

Other oxygenates like ETBE, which is used in France can be expected to evaporate less than MTBE due to its higher boiling temperature and lower vapor pressure but the other environmental aspects are comparable to MTBE.
In the U.S., ethanol will probably substitute MTBE, because it is well degradable in the environment. However, its use shows two significant disadvantages: First, the hygroscopic property of ethanol, that leads to the need of separated storage from gasoline until the delivery to gasoline stations and second, the resulting lower degradation ablility of the gasoline component benzene in groundwater if contaminated by gasoline containing ethanol.

The solutions to air quality problems caused by vehicle emissions should include considerations of other effects on the environment and not simply replacing MTBE with another oxygenate. Life-cycle analysis should be a key element for policy makers [BLUE RIBBON PANEL, 1999; CHANG AND LAST, 1998]. In the case of MTBE versus ethanol, for

example, the relevance of toxicological aspects of the ether (including the formation of TBF, TBA and formaldehyde) and the reduction of CO and hydrocarbon emissions due to the use of MTBE should be compared to the impact of formed amounts of acetaldehyde and possibly PAN from the use of ethanol. Long-term economic aspects cannot be excluded from these considerations. Is it, for example, worth effecting large investigations for the substitution of MTBE by ethanol if technologies with less environmental impact other than commonly used in vehicles emerge?

More research in cleaner-burning engines and cleaner-burning fuels with fewer impurities is needed. Moreover, after the environmental disastrous stories of gasoline additives (tetraethyl lead ✍ aromatics ✍ MTBE ✍ ?) new engine technologies, not depending on the burning of fuel may be the choice of future mobility. The chairman of the EUROPEAN ASSOCIATION OF OXYGENATED FUEL PRODUCERS, H. ROVERS, noted that more research is needed in the new lean burn engine technology, modern diesel engines and fuel cell technology [ROVERS, 2000].

Chemical cocktails of MTBE, antibiotics and endocrinic compounds are released by sewage plants or accidents into river water and nowadays, its concentrations and pathways can be determined by analytical methods. However, the evaluation of effects remains difficult. The increasing number of allergic reactions of humans may be linked to the increasing number of anthropogenic compounds ubiquitiously present in the environment at low concentrations. Recently, the Umweltbundesamt presented the OSPAR-Strategy, which is the result of the decisions of 16 countries to stop the input of dangerous chemicals into the North Atlantic Sea until 2020 [EAWAG, 2001].

However, the most important conclusion drawn from the MTBE story and its predecessors is, that never again, a chemical should be blindly added to a product widely used and dispersed by humans without assessing the future risks for the environment. Even if the toxic effects of MTBE seem low, it is not desirable to have detectable concentrations of a gasoline additive in the compartments that we live on, drinking water, precipitation, river water and air.

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Key Words

English

MTBE, OXYGENATE, ADDITIVE, REFORMULATED GASOLINE, FUEL, SPME, D3MTBE, VOCS, GC, GC/ MS, PRECIPITATION, RAIN, SNOW, URBAN RUNOFF, SURFACE WATER, RIVER WATER, RHINE, MAIN, WASTE WATER, SEWAGE, INDUSTRIAL EFFLUENTS, EQC, COMPARTMENT, PARTITIONING, GERMANY

German

MTBE, OXYGENAT, ADDITIV, VERGASERKRAFTSTOFF, REFORMULIERTES BENZIN, SPME, D3MTBE, LEICHTFLÜCHTIG, GC, GC/ MS, NIEDERSCHLAG, REGEN, SCHNEE, URBAN RUNOFF, OBERFLÄCHENWASSER, OBERFLÄCHENGEWÄSSER, FLUSS WASSER, RHEIN, MAIN, ABWASSER, KLÄRANLAGE, INDUSTRIE, EQC, KOMPARTIMENT, DEUTSCHLAND

Abbreviations

AOS	Adsorbable organic sulphur
AOX	Adsorbable organic halogens
BTEX	Benzene, toluene, ethylbenzene and xylenes
CW/ DVB	Carbowax/ divinylbenzene
d_3MTBE	Deuterated methyl tert-butyl ether
DAI	Direct aqueous injection
DIPE	Di-isopropyl ether
EDTA	Ethylenedinitrilotetraacetic acid
ETBE	Ethyl *tertiary*-butyl ether
EURO II	Directive 94/12/EC
EURO III	Directive 98/70/EC
EURO I	Directive 91/441/EEC
FID	Flame ionization detector
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GC/ MS	Gas chromatography/ mass spectrometry
HPLC	High Pressure Liquid Chromatography
HS-SPME	Headspace-Solid-Phase Microextraction
LT-MDL	Long-term method detection level
LUSTs	Leakage underground storage tanks
MS	Mass spectrometry
MTBE	Methyl *tertiary*-butyl ether
next-TAME	C_4-C_7 *Tertiary* alkyl methly ethers
NMR	Nuclear magnetic resonance spectroscopy
n.n.	nicht nachweisbar, not detected (<10 ng/L)
NTP	National Toxicology Program
O-FID	Oxygen-specific detector
P&T	Purge-and-trap extraction
PAHs	Polycyclic aromatic hydrocarbons
PAN	Peroxyacetyl nitrate

PDMS/ Carboxen	Poly(dimethylsiloxane)/ Carboxen
PDMS/ DVB	Poly(dimethylsiloxane)/ divinylbenzene
PID	Photoionization detector
SIM	Single ion monitoring mode
SPME	Solid-Phase Microextraction
TAME	*Tertiary*-amyl methyl ether
TBA	*Tertiary* butyl alcohol
TBF	*Tertiary* butyl formate
VOCs	Volatile organic compounds
TCE	Trichloroethene
PCE	Tetrachloroethene
CF	Trichloromethane, chloroform
MON	Motor octane number
RON	Research octane number
EQC	Equilibrium criterion
CO	Carbon monoxide
CO_2	Carbon dioxide
NOx	Nitrogen oxides
MAK	Maximale Arbeitsplatzkonzentration
Log K_{OW}	Logarithmic octanol/ water coefficient
Log K_{OC}	Logarithmic water/ organic carbon coefficient
RSD	Relative standard deviation
RFG	Reformulated gasoline (2.0 % w/w of oxygen)
Oxyfuel	Oxygenated fuel (2.7 % w/w of oxygen)
LD_{50}	Concentration where 50 % of the participants died (lethal) in the test

MTBE Web Sites

http://calepa.ca.gov/programs/mtbe
http://geotracker.llnl.gov/
http://ofa.net
http://trg.ucdavis.edu/clients/trg/research/mtbe.html
http://tsrtp.ucdavis.edu/mtbe
http://umweltbundesamt.de
http://water.wr.usgs.gov/mtbe/
http://www.acwanet.com/legislation/regulatory/mtbe2.html
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http://www.api.org/ehs/mtbelink.htm
http://www.api.org/ehs/othrmtbe.htm
http://www.efoa.org
http://www.epa.gov/oms/consumer/fuels/oxypanel/blueribb.htm
http://www.epa.gov/oms/regs/fuels/oxy-area.pdf
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http://www.epa.gov/OST/Tools/dwstds.html
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http://www.swrcb.ca.gov/baydelta/mtbe_finaldraft.doc
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http://wwwsd.cr.usgs.gov/nawqua/vocns/mtbe/bib/key.html

APPENDIX

Measured Environmental Methyl *tert*-Butyl Ether (MTBE) Concentrations (ng/L)

Precipitation

Sampling Date	Frankfurt/M	Sampling Date	Frankfurt/M	Sampling Date	Frankfurt/M
12/07/98	53	07/01/00	<10	12/14/00	<10
12/15/98	70	07/24/00	<10	12/22/00	12
03/22/99	<10	08/19/00	<10	12/27/00	24
03/29/99	<10	09/06/00	34	12/28/00	43
06/10/99	<10	09/13/00	<10	01/02/01	75
07/19/99	<10	09/20/00	41	01/05/01	24
08/18/99	13	10/12/00	36	01/10/01	12
09/23/99	16	10/19/00	33	01/11/01	66
10/01/99	21	10/23/00	80	01/24/01	40
11/20/99	29	10/25/00	11	01/28/01	11
12/15/99	40	10/27/00	17	02/03/01	23
01/05/00	<10	10/31/00	<10	02/06/01	12
02/01/00	<10	11/01/00	85	02/07/01	13
03/01/00	<10	11/06/00	<10	02/13/01	74
03/06/00	<10	11/13/00	45	02/22/01	70
04/29/00	<10	11/17/00	22	02/28/01	10
05/01/00	<10	11/23/00	<10	03/01/01	64
05/17/00	<10	12/05/00	31	03/09/01	34
06/22/00	<10	12/12/00	14	03/12/01	<10

	November	December	January	February
Bonn	35	14	<10	42
Köln	44	13	36	-
Hamburg	14	-	40	<10
Stuttgart	15	13	<10	61
Berlin	40	21	30	15
Frankfurt/Main	30	22	43	34
Westerland/ Sylt	<10	<10	<10	<10
Zingst	<10	<10	<10	<10
Neuglobsow	<10	<10	18	58
Waldhof	<10	<10	<10	<10
Schmücke	<10	<10	22	<10
Deuselbach	<10	<10	18	21
Schauinsland	<10	<10	<10	<10
Brotjacklriegel	<10	<10	<10	<10
Feldberg/ Taunus	-	15	11	-
Rade	<10	<10	18	<10
Altenholz-Klausdorf	<10	<10	54	<10

Main River

Sampling Date	Frankfurt/M City	Frankfurt/M-Nied	Bischofsheim Right Shore	Bischofsheim Left Shore
01/14/99	10	-	-	-
04/21/99	13	-	-	-
05/26/99	116	-	-	-
06/23/99	33	-	-	-
07/27/99	51	-	-	-
08/20/99	19	-	-	-
10/15/99	33	-	-	-
11/01/99	40	-	-	-
11/18/99	95	-	-	-
12/08/99	10	-	-	-
12/14/99	21	-	-	-
01/28/00	31	-	-	-
02/17/00	26	-	-	-
03/17/00	13	-	-	-
04/06/00	22	-	-	-
04/28/00	80	-	-	-
05/13/00	367	-	-	-
05/15/00	151	-	-	-
06/15/00	181	-	-	-
07/13/00	-	-	169	197
07/18/00	21	-	-	-
08/09/00	-	389	322	297
08/23/00	221		406	220
08/28/00	-	457	223	272
08/30/00	367	-	-	-
09/06/00	-	122	199	126
09/13/00	359	-	-	-
09/20/00	-	112	213	176
10/04/00	-	153	189	134
10/11/00	88	-	-	-
10/19/00	-	64	116	59
10/23/00	-	220	504	427
10/24/00	152	-	-	-
11/08/00	-	25	51	27
11/11/00	28	-	-	-
11/15/00	-	42	185	92
11/19/00	36	-	-	-
11/27/00	71	-	-	-
11/29/00	-	-	-	147
12/05/00	255	-	-	-
12/13/00	502	-	-	-
12/17/00	122	-	-	-
12/28/00	104	-	-	-
01/04/01	106	-	-	-
01/10/01	-	-	-	53
01/12/01	49	-	-	-
01/15/01	-	-	-	73
01/20/01	34	-	-	-
01/28/01	66	-	-	-
02/05/01	33	-	-	-
02/07/01	-	-	-	182
02/12/01	-	-	-	
02/13/01	182	-	-	-
02/21/01	308	832	535	547
03/01/01	66	-	-	-

Sampling Location	09/19-22/00	01/16-18/01
Main km 1.3 middle	130	-
Main km 4.5 right	275	-
Main km 4.5 left	158	-
Main km 4.5 middle	-	87
Main km 10 middle	-	90
Main km 14,5 middle	-	77
Main km 16 middle	-	68
Main km 22 right	67	54
Main km 22 left	158	-
Main km 22 middle	-	59
Main km 24,2 middle	-	64
Main km 26 middle	-	60
Main km 34 middle	-	43
Main km 40 middle	-	40
Main km 46 middle	-	65
Main km 54 middle	-	53
Main km 56 middle	-	65
Main km 66 mix	-	31
Main km 77 mix	-	25
Main km 77 right	148	-

Sampling Date	Sampling Location	
08/30/00	Offenbach	241
08/30/00	Gerbermühle	363
08/30/00	Frankfurt/ M	367
08/30/00	Niederrad	362
08/30/00	Kelsterbach	294
08/30/00	Rüsselsheim	323
08/30/00	Bischofsheim	362
08/30/00	Gustavsburg	406

Elbe River

Sampling Date	Sampling Location	
09/02/00	Boitzenburg	<10
09/02/00	Lauenburg	30
09/02/00	Tesperhude	48
09/02/00	Geesthacht	31
09/02/00	Winsen	36
09/02/00	Meckelfeld/ Over	<10
09/02/00	Hamburg Landungsbrücken	76
09/02/00	Hamburg Blankenese	87
09/02/00	Stade/ Stadersand	37
09/02/00	Stade/ Abbenfleth	22
09/02/00	Wedel/ Schulau	65
09/02/00	Groß-Kollmar	<10
09/02/00	Wischhafen	24
09/02/00	Glückstadt	30
03/28/99	Dresden	123
10/20/00	Hamburg-Neuenfelde	155
10/19/00	Hamburg-Elbbrücken	34
11/18/00	Hamburg-Neuenfelde	<10
04/22/99	Hamburg Harbour	21
10/18/99	Hamburg Harbour	<10
01/11/01	Hamburg Harbour	59
02/14/01	Hamburg Harbour	101

Rhine River

Sampling Date	Mainz/ Wiesbaden	Sampling Date	Mainz/ Wiesbaden
03/21/99	160	10/19/00	252
05/11/00	131	10/23/00	334
06/06/00	167	10/24/00	246
08/01/00	392	10/30/00	287
08/17/00	448	11/06/00	295
08/21/00	230	11/13/00	310
08/28/00	324	11/20/00	269
08/30/00	378	11/27/00	277
09/04/00	107	12/04/00	309
09/05/00	150	12/11/00	307
09/11/00	293	12/18/00	321
09/18/00	441	12/21/00	579
09/20/00	406	01/02/01	311
09/25/00	258	01/08/01	194
09/29/00	322		

Sampling Date	Sampling Location	
11/07/00	Schaffhausen	23
11/07/00	Waldshut-Tiengen	195
11/07/00	Rheinfelden	46
11/07/00	Müllheim-Neuenburg	13
11/07/00	Breisach	21
11/07/00	Lahr/Rhinau	92
11/07/00	Gambsheim	142
11/07/00	Rastatt-Plittersdorf	138
11/07/00	Leopoldshafen	383
11/07/00	Schwetzingen-Koller	187
11/07/00	Worms	137
11/07/00	Gernsheim	203
11/06/00	Mainz-Laubenheim	350
11/06/00	Mainz-Heidesheim	339
11/06/00	Oberwesel	307
11/06/00	Boppard	236
11/06/00	Weißenthurm	52
11/06/00	Bad Breisig	69
11/06/00	Bonn-Auerberg	119
11/06/00	Wesseling	191
11/06/00	Zons	234
11/06/00	Mündelheim	216
11/06/00	Wesel	218

Sampling Date	Sampling Location	
03/21/99	Nierstein	136
09/03/00	Cologne	227
11/08/00	Harbour Gernsheim	163
06/13/00	Geinsheim	256
08/17/00	Geinsheim	187
09/20/00	Rhine/ km 425 middle	123
09/20/00	Rhine/ km 450 left	394
09/20/00	Rhine/ km 456 right	90
10/26/00	Rhine/ km 480	246
09/20/00	Rhine/ km 527 middle	134
09/20/00	Rhine/ km 543 middle	122

Urban Creeks in the Vicinity of Frankfurt/M

Sampling Date	Lahn/ Oberbiel	Schwarzbach/ Trebur	Nidda/ Nied	Kinzig/ Hanau	Landgraben/ Trebur
07/12/00	-	72	-	-	50
08/09/00	65	69	62	59	-
08/23/00	26	495	25	25	-
08/28/00	163	77	14	32	-
09/06/00	<10	182	<10	19	-
09/11/00	89	92	<10	<10	-
09/20/00	13	86	<10	<10	-
10/04/00	49	38	12	17	-
10/19/00	58	172	22	16	-
10/23/00	34	794	43	90	2258
11/08/00	22	363	<10	22	-
11/15/00	47	195	<10	<10	-
11/19/00	66	-	-	-	107
11/29/00	-	-	76	1099	-
01/10/01	-	245	87	37	2267
01/15/01	-	1024	47	45	-
02/07/01	43	155	42	36	-
02/12/01	36	133	41	33	-
02/21/01	34	87	56	39	-
02/21/01	524	748	308	96	81
03/01/01	494	353	66	88	55

Urban Creek: Lahn

	Sampling Location			
	Coelbe	Lahnau	Oberbiel	Limburg-Staffel
06/13/00	12	127	-	293
08/09/00	-	-	65	-
08/14/00	-	-	278	-
08/16/00	-	48	-	172
08/22/00	10	-	26	-
08/28/00	-	-	163	-
09/06/00	-	-	<10	-
09/11/00	-	-	89	-
09/20/00	-	-	13	-
10/04/00	-	-	49	-
10/19/00	-	-	58	-
10/23/00	-	-	34	-
10/26/00	-	-	-	109
11/02/00	-	-	22	-
11/15/00	-	-	47	-
11/19/00	-	-	66	-
11/27/00	-	-	-	<10
02/07/01	-	-	43	-
02/12/01	-	-	36	-
02/21/01	-	-	34	-

Other Rivers and Rural Creeks

Sampling Date	Sampling Location	
03/10/99	Oder/ Frankfurt	10
06/13/00	Hengstbach/ Zeppelinheim	<10
08/08/00	Weschnitz/ Biblis	48
08/28/00	Usa/ Bad Nauheim, upstream	<10
08/28/00	Usa/ Bad Nauheim, downstream	<10
09/02/00	Wümme/ Ottersberg	19
09/02/00	Hunte/ Wildeshausen	<10
09/02/00	Este/ Hollenstedt	<10
09/02/00	Ruhr/ Westhofen	21
09/02/00	Luhe/ Winsen	<10
09/02/00	Ems/ Greven	21
09/02/00	Oste/ Sittensen	<10
09/28/00	Weser/ Hemeln	89
08/21/00	Fulda/ Bad Hersfeld	<10
09/27/00	Fulda/ Hann. Münden	142
09/06/00	Neckar/ km 2.2	15
10/07/00	Donau/ Deggendorf	<10
10/07/00	Donau/ Regensburg	<10
10/07/00	Donau/ Straubing	<10
10/07/00	Schwarzer Regen/ Zwiesel	<10
10/07/00	Isar/ Plattling	<10
10/07/00	Naab/ Effertshausen	<10
09/01/00	Kieler Förde/ Yachthafen Kiel	<10
10/22/00	Kieler Förde/ Yachthafen Kiel	<10
06/13/00	Rodau/ Mühlheim	198
08/17/00	Rodau/ Mühlheim	34
11/09/00	Rodau/ Mühlheim	16
06/13/00	Geräthsbach/ Mörfelden	51
10/23/00	Geräthsbach/ Mörfelden	32
06/13/00	Gundbach/ Mörfelden	18
10/23/00	Gundbach/ Mörfelden	19
09/26/00	Modau/ Stockstadt	30
10/24/00	Modau/ Stockstadt	18
06/13/00	Gersprenz/ Babenhausen	35
10/18/00	Gersprenz/ Babenhausen	19
06/13/00	Dill/ Wetzlar	30
11/27/00	Dill/ Wetzlar	<10
06/13/00	Diemel/ Bad Karlshafen	14
11/29/00	Diemel/ Bad Karlshafen	<10
06/13/00	Ohm/ Cölbe	14
08/22/00	Ohm/ Cölbe	<10
08/21/00	Haune/ Bad Hersfeld	<10
11/29/00	Haune/ Bad Hersfeld	<10
09/25/00	Schwalm/ Felsberg	<10
11/29/00	Schwalm/ Felsberg	<10
11/29/00	Werra/ Wilzenhausen	<10
11/06/00	Lippe/ Wesel	736

Channels

Channel/River and Location	Sampling Date	River	Channel
Weser (Bremen) and Mittellandkanal (Bramsche)	02/09/00	162	204
Elbe and Elbe-Lübeck-Kanal (Lauenburg)	02/09/00	30	55
Rhine and Grand Canal d'Alsace (Müllheim)	11/07/00	13	127
Lippe and Wesel-Datteln-Kanal (Wesel)	11/06/00	736	28
Main-Donau-Kanal/ Erlangen	10/07/00	-	48
Datteln-Hamm-Kanal/ Hamm	02/09/00	-	35

Urban Runoff

Sampling Date	
09/06/00	118
09/06/00	51
09/13/00	139
09/13/00	147
10/12/00	1174
10/27/00	91
10/27/00	84
11/02/00	172
11/02/00	110
11/02/00	73
12/19/00	30
12/19/00	264

Industrial Effluents in the Vicinity of Frankfurt/M

Sampling Date	Company No.	
06/13/00	1	14
10/23/00	1	<10
08/23/00	2	<10
11/08/00	2	<10
01/25/01	2	12397
08/24/00	3	<10
01/22/01	3	40
08/31/00	4	183
01/23/01	4	28422
08/31/00	5	173
08/30/00	6	53
01/25/01	6	49
01/23/01	7	53
01/22/01	8	20
08/31/00	9	127
01/24/01	9	1814
01/24/01	9	<10
01/24/01	9	361
01/24/01	9	185

Sewage Plants Frankfurt/M-Niederrad and Sindlingen

Sampling Date	Effluent of sewage plant Niederrad	Influent "Griesheim" of sewage plant Niederrad	Influent "Niederrad" of sewage plant Niederrad	Influent of sewage plant Sindlingen	Effluent of sewage plant Sindlingen
11/11/00	<10	32	181	47	-
11/19/00	14	24	140	133	-
11/27/00	76	70	137	21	-
12/05/00	255	138	709	136	-
12/13/00	642	63	170	46	-
12/17/00	104	51	74	30	-
12/28/00	78	196	1268	277	-
01/04/01	108	291	529	277	-
01/12/01	57	296	351	211	-
01/20/01	40	171	251	362	-
01/28/01	64	262	299	87	-
02/05/01	35	273	217	86	-
02/13/01	430	325	332	574	356
02/21/01	1229	524	748	96	81
03/01/01	829	494	353	88	55

Degradation of MTBE in Main Water

Sampling Date	Day	4 °C	18 °C
08/23/00	1	221	218
08/29/00	7	214	212
09/11/00	20	204	215
09/19/00	28	209	218
10/04/00	43	207	213
10/17/00	56	203	197
10/30/00	69	211	165
11/18/00	88	192	152
12/07/00	107	170	104
12/31/00	131	165	98
03/01/01	181	160	70
08/17/01	350	125	10

Riverbank Filtration and Drinking Water

Sampling Date	Rhine River	Riverbank Filtration at Rhine River (Distance from Bank) 18 m (A)	39 m (B)	79 m (C)
02/13/01	178	133	116	64
02/13/01	178	133	120	71
02/13/01	178	91	129	104

Sampling Date	Water Utility at Rhine River	Sample	
02/07/01	1	Recovering Well Water B	99
02/07/01		Recovering Well Water 3	117
02/07/01		Raw Water	111
02/07/01		Drinking Water	43
02/08/01	2	Recovering Well Water 2	71
02/08/01		Raw Water	86
02/08/01		Drinking Water 1	62
02/08/01		Drinking Water 2	110
02/12/01	3	Recovering Well Water 1	61
02/12/01		Recovering Well Water 6	69

	Riverbank Filtration at Main River (Well No.)			
Sampling Date	**1123**	**1184**	**1128**	**1132**
November 1999	52	77	12	<10
April 2000	37	101	13	<10
November 1999/ April 2000	-	-	-	-
January 2001	131	-	-	-
January 2001	-	-	-	-
May 2001	238	250	29	<10
May 2001	-	-	-	-

Lebenslauf

Name	Christine Achten, geb. Eichler
Geburtsdatum	17.12.69
Geburtsort	Buchholz in der Nordheide
Familienstand	verheiratet, ein Kind

Schulausbildung	1989	Abitur am Gymnasium Neu Wulmstorf/ Hamburg

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Hochschulausbildung	10/90 - 02/93	Grundstudium, Universität Bonn
	04/93 - 03/95	Hauptstudium, RWTH Aachen freiwillige Studienarbeit: *PAK - Belastungsmuster in Flußsedimenten und ihre Transportwege zur Ermittlung der Emissionsquellen - Beispiel Aachener Raum –* Prof. Dr. W. Püttmann
	03/95 - 05/97	Diplom, RWTH Aachen Prüfungsfächer Ingenieurgeologie und Petrologie Diplomarbeit: *Wechselwirkungen zwischen LCKW-Abbau und Hydrochemie im Grundwasserabstrom ausgewählter Altstandorte in Düsseldorf* Prof. Dr. W. Püttmann
	seit 05/1997	Promotion am Institut für Mineralogie - Umweltanalytik -, Universität Frankfurt am Main Promotionsthema: *Methyl tert-butyl ether (MTBE) in the aquatic environment in Germany* Prof. Dr. W. Püttmann und Prof. Dr. H. F. Schöler

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Berufsweg	07/91 - 09/91	Steinfeld & Partner Umwelttechnik, Hamburg
	03/93 - 08/93	Landschafts-, Archäologie- und Naturdenkmalpflege, Aldenhoven
	01/94 - 12/94	Lehrstuhl für Geologie, Geochemie und Lagerstätten des Erdöls und der Kohle, RWTH Aachen
	01/95 - 01/96	Hydrogeologisches Ingenieurbüro Olzem, Aachen
	07/96	Analytisches Labor Aachen (ALA)
	03/96 - 04/97	Geologisches Ingenieurbüro GEOBIT, Aachen
	05/97 - 03/02	Institut für Mineralogie -Umweltanalytik-, Universität Frankfurt am Main
	01/99 - 12/00	ARCADIS Consult GmbH, Darmstadt
	ab 03/02	Altenbockum und Partner, Geologen, Aachen